

Di- and Trivalent Organogermanium Reactive Intermediates. Kinetics and Mechanisms of Some Reactions of Diphenylgermylene and Tetraphenyldigermene in Solution

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Abstract: The reactivity of diphenylgermylene (Ph_2Ge) with several classes of germylene scavengers has been studied in hexane solution at 23 °C by laser flash photolysis of 3,4-dimethyl-1,1-diphenyl-1-germacyclopent-3-ene (**1a**), a clean and highly efficient precursor to the germylene and its dimer, tetraphenyldigermene (**2a**). The reactions studied include M–H insertion reactions with Group 14 hydrides ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$), halogen atom abstractions from bromo- and chlorocarbons, Lewis acid–base complexation with 1°, 2°, and 3° aliphatic amines, and reaction with an aliphatic alkene, alkyne and diene, and oxygen. Absolute rate constants for (irreversible) scavenging of the germylene could be obtained by direct measurement of the germylene decay kinetics for all but the least efficient scavengers (triethylsilane, oxygen, chloroform, and 1-bromopentane), for which estimates of the rate constants were obtained by Stern–Volmer analysis of the reduction in digermene yield as a function of scavenger concentration. Distinctly different kinetic behavior is observed for scavenging of Ph_2Ge by isoprene, 4,4-dimethyl-1-pentene, and triethylamine; in these cases, the results suggest that reaction is rapid ($k_{\text{Q}} = 3\text{--}6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) but reversible ($K_{\text{eq}} = 2500\text{--}ca. 20,000 \text{ M}^{-1}$) over the range of scavenger concentrations studied. The reactions with the C–C unsaturated compounds proceed via the intermediacy of long-lived transient species absorbing at $<290 \text{ nm}$, which are tentatively assigned to the corresponding three-membered germanocycles on the basis of their UV spectra and lifetimes. Upper limits for the absolute rate constants for reaction of tetraphenyldigermene (**2a**) toward many of these reagents are also reported.

Introduction

There has been considerable interest over the last few decades in the chemistry of the heavy Group 14 analogues of carbenes (silylenes,^{1–3} germylenes,^{3–9} and stannylenes^{3,5,7–9}) and a great deal is now known of their rich reactivities. Much of this knowledge has evolved relatively recently, from the study of isolable derivatives bearing sterically or electronically stabilizing substituents at the M^{II} center. Early work focused on the chemistry of simpler, transient derivatives, generated by thermolysis or photolysis of appropriate precursors.^{5,8} Silylenes and germylenes, which have been most extensively studied, exhibit marked similarities in their chemistries and to the chemistry of singlet carbenes. Their typical reactions include dimerization

to the corresponding $\text{M}=\text{M}$ doubly bonded species (disilenes or digermenes), X–H insertion reactions with hydroxylated or aminated substrates and Group 14 (Si and Ge) hydrides, addition to C–C and C–X multiple bonds, halogen-atom abstraction or carbon–halogen insertion, etc.^{3–5} They are potent electrophiles, forming Lewis acid–base complexes with ethers, amines, phosphines, and sulfides. Such complexation is known to mediate their reactivities by suppressing dimerization and further oligomerization, which usually leads ultimately to complex mixtures of products.⁵

Despite the existence of a wealth of information on the synthetic and preparative aspects of their chemistry, relatively little is known of the kinetics and mechanisms of the reactions of simple germylenes in solution,⁸ and what is known has for the most part been obtained through competition kinetic methods and/or product studies. The largest body of kinetic data exists for the parent molecule (H_2Ge), which has been studied in the gas phase by laser flash photolysis methods.^{9–21} Detailed kinetic

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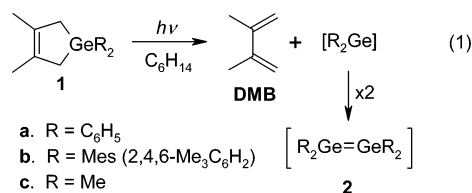
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studies—often interpreted mechanistically with the aid of high level theoretical calculations—have been reported for its reactions with a wide variety of substrates, including ethylene^{16,22} and other simple alkenes,^{10,15} acetylene,^{10,19,21} 1,3-butadiene,¹⁰ hydrosilanes,^{10,12,14,19} and -germanes,^{11,17–19} water and methanol,²⁰ dimethyl ether,²⁰ and oxygen.¹⁰ Reliable gas-phase kinetic data have also been reported for Me₂Ge, though much less extensively than for the parent molecule.^{9,17,23}

On the other hand, relatively few absolute rate constants have been determined for dialkyl- and diarylgermylenes in solution. In the case of Me₂Ge, for example, the list is limited to those for reaction with aliphatic dienes, carbon tetrachloride, triethylsilane, and oxygen, and the level of agreement between the various studies is relatively poor.^{24–28} This is true of not just the kinetics, but also of the basic spectroscopic properties of the species, which has been reported to exhibit UV absorption maxima ranging from 320 to 490 nm depending on the precursor.⁸ Much better success has been obtained with dimesitylgermylene (Mes₂Ge), for which there is very good agreement on the UV/vis spectrum measured by different groups from at least four different precursors, both in solution and in hydrocarbon matrixes at low temperatures.^{29–32} Nevertheless, the list of reactions that have been studied is still quite limited.³¹

Recently, we reported the results of a study of the photochemistry of two “new”³³ diarylgermylene precursors (**1a** and **1b**) in hexane solution by steady state and laser flash photolysis methods (equation 1).³² Trapping experiments with a number of different germylene scavengers showed that photolysis of these molecules proceeds extremely cleanly, producing 2,3-dimethyl-1,3-butadiene (DMB) and the expected trapping products of Ph₂Ge and Mes₂Ge, respectively, as the only detectable products even at quite high conversions of substrate. The photochemistry is also remarkably efficient; Ph₂Ge is formed with a quantum yield $\Phi = 0.62$ upon irradiation of **1a** in deoxygenated methanolic hexane solution with 254 nm light.³² The photolysis of these compounds, as well as the tetramethyl derivative (**1c**), is sufficiently clean and efficient for the

corresponding germylens and their Ge=Ge doubly bonded dimers (**2**) to be detected and characterized by laser flash photolysis in hexane solution. The transient assignments were corroborated by time-dependent DFT calculations of the UV absorption spectra of the three germylens and the corresponding digermene dimers, and by preliminary studies of the kinetics of the reactions of the two diarylgermylenes with *n*-butylamine (BuNH₂) and acetic acid (AcOH), both potent germylene scavengers.



In this paper, we describe the results of an exploratory laser flash photolysis study of the reactivity of Ph₂Ge with a variety of representative germylene scavengers, and report absolute rate constants for its reaction with aliphatic amines, halocarbons, an aliphatic alkyne, diene and an alkene, oxygen, acetic acid, and the Group 14 hydrides R₃MH (M = Si, Ge, Sn; R = ethyl or *n*-butyl) in hexane solution. The expected primary products of these reactions, as established by earlier work on Ph₂Ge^{32,33} or other transient germylens,^{3–5} are shown in Scheme 1; of the scavengers selected for study (see Chart 1), only BuNH₂,³² AcOH,³² Et₃SiH,³² isoprene,^{32,33} and CCl₄³⁴ have yet been specifically characterized with product studies in the case of Ph₂Ge. The others were selected for the purposes of comparison to existing gas- and/or solution-phase kinetic data for the reactions of other transient germylens, either with them specifically (e.g., C₅H₁₁Br,³¹ Et₃GeH,¹⁸ O₂^{10,23,31}) or with simpler

Scheme 1

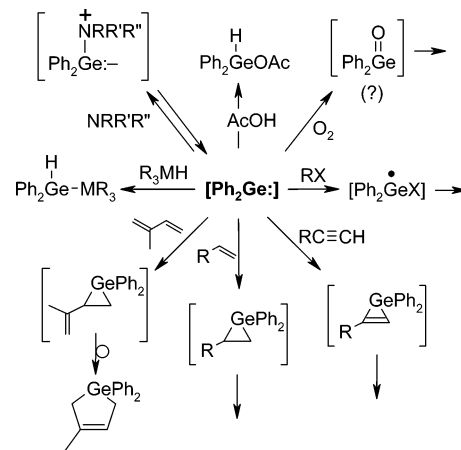
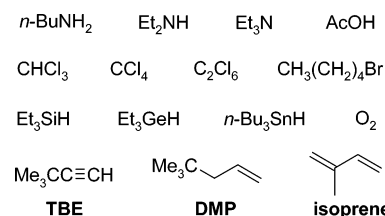


Chart 1



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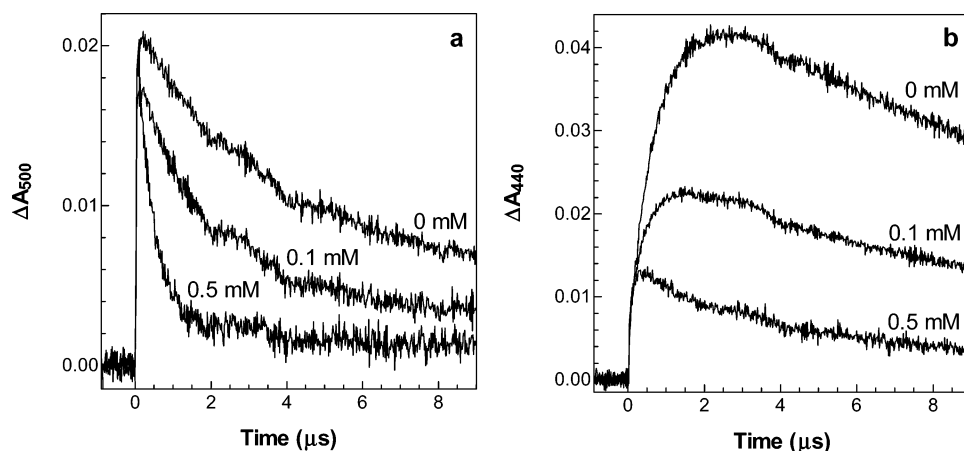


Figure 1. Effects of added Bu_3SnH on the transient absorptions due to (a) Ph_2Ge and (b) **2a** recorded at 500 and 440 nm, respectively.

analogues (e.g., the alkyne and the alkene), or in the interest of exploring the variations in reaction kinetics with structure within a given class of scavenger. Absolute rate constants for reaction of the same reagents with tetraphenyldigermene (**2a**) have also been determined or estimated where possible.

Results

Laser flash photolysis experiments with **1a** were carried out in dry, deoxygenated hexane solution using a $7 \times 7 \text{ mm}^2$ flow cell to continuously refresh the solutions between laser pulses, which were delivered by a KrF excimer laser (248 nm, ca. 25 ns, ca. 100 mJ) of the appropriate intensity to produce initial transient concentrations on the order of $15\text{--}25 \mu\text{M}$. As previously reported,³² laser photolysis of **1a** results in the prompt formation of Ph_2Ge ($\lambda_{\text{max}} = 500 \text{ nm}$; $\epsilon_{\text{max}} = 1650 \text{ M}^{-1}\text{cm}^{-1}$), whose decay occurs over several microseconds and follows second-order kinetics, concomitantly with the growth of absorptions due to tetraphenyldigermene (**2a**; $\lambda_{\text{max}} = 440 \text{ nm}$), which then decays over ca. $50 \mu\text{s}$ with predominant second order kinetics. Transient absorptions recorded at 500 nm are mainly due to Ph_2Ge , superimposed on tail absorptions due to **2a**.

Addition of most of the reagents of Chart 1 resulted in reductions in the maximum intensity of the signals due to the digermene ($(\Delta A_{440})_{\text{max}}$, measured at the peak of the 440 nm growth/decay profile), shortening of the digermene growth time, and acceleration of the germylene decay, each to an extent that increased with the concentration of added reagent. The germylene decays (measured at 500–530 nm) fit acceptably to clean pseudo-first-order kinetics once sufficient reagent was added to reduce the maximum signal intensity due to the digermene to less than ca. 30% of its value in pure hexane solution. Figure 1 shows examples of typical behavior of the transient absorptions due to Ph_2Ge (at 500 nm) and **2a** (at 440 nm), recorded for solutions containing Bu_3SnH over the 0–0.5 mM concentration range. It should be noted that in the presence of 0.5 mM of this scavenger, the maximum intensity of the digermene signal is reduced to ca. 25% of its value in pure hexane solution, and it remains detectable in the 500 nm (germylene) decay trace as a slowly decaying residual absorption (see Figure 1a). The germylene signal decays cleanly to the pre-pulse level (within our detection limits) in traces recorded for solutions containing 0.8 mM of the reagent or higher.

Table 1. Absolute Rate (k_Q) and Stern–Volmer Constants (K_{SV}) for Reactions of Diphenylgermylene (Ph_2Ge) in Dry, Deoxygenated Hexane Solution at $23 \pm 1 \text{ }^\circ\text{C}^a$

reagent	$k_Q/10^6 \text{ M}^{-1}\text{s}^{-1b}$	$K_{\text{SV}}/\text{M}^{-1c}$
Ph_2Ge	11000 ± 2000^d	
BuNH_2	10100 ± 600^d	14130 ± 980
Et_2NH	7290 ± 900	10650 ± 1200
Et_3N	2800 ± 900	1400 ± 240
AcOH	3900 ± 700^d	7130 ± 650
CCl_4	10.9 ± 0.4	18.7 ± 2.6
C_2Cl_6	4.1 ± 0.1	10.3 ± 0.4
CHCl_3	$(0.20 \pm 0.04)^e$	0.24 ± 0.02
$\text{C}_5\text{H}_{11}\text{Br}$	$(4.2 \pm 0.8)^e$	5.0 ± 1.2
O_2	$(27 \pm 6)^e$	31.7 ± 12
Et_3SiH	$(0.56 \pm 0.09)^e$	0.67 ± 0.05
Et_3GeH	27.9 ± 1.6	33.3 ± 2.5
Bu_3SnH	$3,490 \pm 90$	5370 ± 170
$\text{HC}\equiv\text{CCMe}_3$ (TBE)	5180 ± 470	7500 ± 600
$\text{H}_2\text{C}=\text{CHC}(\text{Me})=\text{CH}_2$ (isoprene)	5500 ± 1200	1970 ± 150
$\text{H}_2\text{C}=\text{CHCH}_2\text{CMe}_3$ (DMP)	4200 ± 200	1500 ± 450

^a Measured by laser flash photolysis of ca. 0.003 M solutions of **1a**. Errors are listed as $\pm 2\sigma$ from least-squares analysis of data according to eqs 2 or 3. ^b From plots of the pseudo-first-order decay rate constants (k_{decay}) of the germylene absorptions at 500 or 530 nm (Ph_2Ge) vs $[\text{Q}]$, at sufficiently high concentrations of $[\text{Q}]$ that the yield of digermene is less than 30% of its value in the absence of the scavenger. ^c From (Stern–Volmer) plots of $[(\Delta A_{440})_{\text{max}}]_0/[(\Delta A_{440})_{\text{max}}]_{[\text{Q}]}$ vs $[\text{Q}]$ according to eq 3. ^d From ref 32. ^e Estimated from the K_{SV} -value, using K_{SV} and k_Q for Et_3GeH quenching as the standard.

Analogous behavior was observed for all of the scavengers studied in this work except for the alkene (DMP), isoprene, and Et_3N , as discussed below. In most cases, the reagent also had the effect of accelerating the decay of the signal due to **2a** over the reagent concentrations where it could be detected, consistent with reaction of the trapping agent with the digermene as well.

Absolute rate constants for reaction of Ph_2Ge with these reagents (Table 1) were determined from plots of the pseudo-first-order rate constants for germylene decay (k_{decay}) vs concentration according to eq 2, where k_0 is the (hypothetical) pseudo-first-order rate constant for germylene decay in the absence of added scavenger (Q), and k_Q is the bimolecular rate constant for the reaction. Plots of k_{decay} vs $[\text{Q}]$ exhibited excellent linearity in every case, as illustrated in Figure 2a for quenching of Ph_2Ge by Et_2NH and Bu_3SnH . These data were obtained over the “high” concentration range where sufficient scavenger was present to reduce the apparent yield of **2a** (as measured by its maximum ΔA value at 440 nm) to $<20\%$ of its value in the

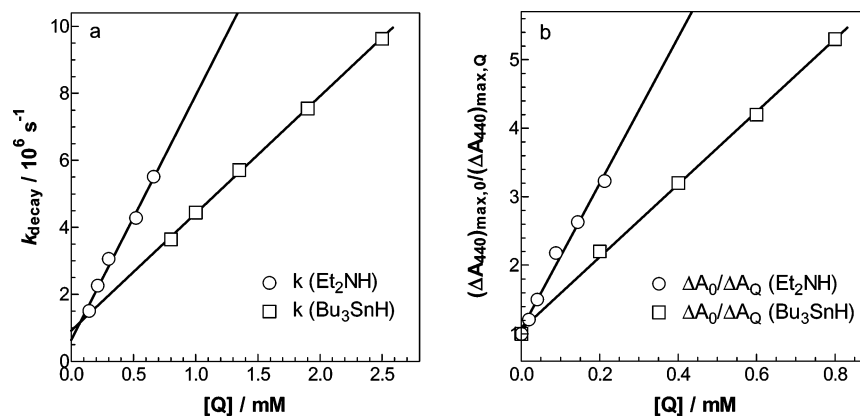


Figure 2. The effects of added Et_2NH (○) and Bu_3SnH (□) on (a) the pseudo-first-order decay rate constant of Ph_2Ge , monitored at 530 nm, and (b) the maximum transient absorbance due to **2a**, monitored at 440 nm (see eq 3). Note the difference in the concentration ranges over which the data in (a) and (b) were recorded.

absence of Q (i.e., >80% quenching), to ensure that the decay of the germylene is dominated by reaction with the scavenger.

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

With some of the less reactive scavengers (Et_3SiH , O_2 , CHCl_3 , and $\text{C}_5\text{H}_{11}\text{Br}$), addition of the reagent resulted in decreases in the maximum signal intensity of the digermene and significant acceleration of the germylene decay, but digermene formation could not be eliminated even at the highest concentrations of reagent that could be added. This limit is defined either by the solubility limit of the reagent in hexane solution or the onset of appreciable screening of the excitation light by the scavenger (which reduces the intensities of the observed signals). As a result, the decay of the germylene followed mixed pseudo-first and second-order kinetics at all scavenger concentrations that could be studied (as revealed by decay traces recorded at 530 nm), and thus absolute rate constants could not be determined reliably by direct measurement in these cases.

Plots of the relative maximum intensities of the digermene signals at 440 nm in the absence and presence of added Q $[(\Delta A_{440})_{\text{max},0} / (\Delta A_{440})_{\text{max},Q}]$ were approximately linear in every case, suggesting adherence to the conventional Stern–Volmer relationship of eq 3, where K_{SV} is the Stern–Volmer constant. Representative examples are shown in Figure 2b for quenching by Et_2NH and Bu_3SnH over the 0–0.2 and 0–0.8 mM concentration ranges, respectively. The resulting K_{SV} -values (corrected, when necessary, for screening of the excitation light by the added reagent, and all determined using roughly the same laser intensity) are listed in Table 1 along with the absolute rate constants determined by direct monitoring of the germylene decays. As can be seen from the data, the trend in K_{SV} values parallels that in k_Q for those scavengers for which both quantities could be determined in all cases but Et_3N , isoprene, and DMP. This is illustrated more clearly in Figure 3, which shows a plot of relative K_{SV} and k_Q values for the germylene scavengers reported in Table 1, calculated using Et_3GeH as the standard scavenger (i.e., $K_{\text{SV}}^{\text{rel}} = K_{\text{SV}}^Q / K_{\text{SV}}^{\text{Et}_3\text{GeH}}$; $k_Q^{\text{rel}} = k_Q / k_{\text{Et}_3\text{GeH}}$). Ignoring the points for Et_3N , isoprene, and DMP for the moment, the correlation for the other scavengers is clearly good enough to allow those absolute rate constants which cannot be measured directly to be estimated with reasonable precision from the Stern–Volmer constants, using Et_3GeH as the standard. The absolute rate constants reported in Table 1 for scavenging by

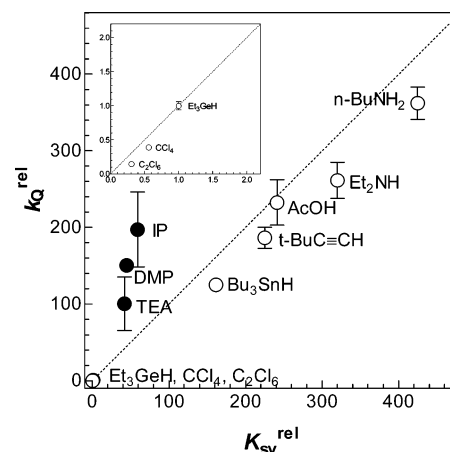


Figure 3. Plot of $k_Q^{\text{rel}} (= k_Q / k_{\text{Et}_3\text{GeH}})$ vs $K_{\text{SV}}^{\text{rel}} (= K_{\text{SV}}^Q / K_{\text{SV}}^{\text{Et}_3\text{GeH}})$ for scavenging of Ph_2Ge by the reagents listed in Table 1, with an expansion of the plot for the least reactive scavengers in the series shown in the Inset; the dotted lines correspond to a slope of 1.0, or a perfect 1:1 correspondence. The solid points are for the reversible scavengers (see text).

Et_3SiH , O_2 , CHCl_3 , and $\text{C}_5\text{H}_{11}\text{Br}$ were thus estimated in this way. These values should be considered upper limits, possibly in excess of the true values by as much as ca. 50%.

$$[(\Delta A_{440})_{\text{max},0} / (\Delta A_{440})_{\text{max},Q}] = 1 + K_{\text{SV}}[Q] \quad (3)$$

Both the good linearity exhibited by the Stern–Volmer plots and the fact that the resulting K_{SV} -values correlate as well as they do with k_Q -values are intuitively reasonable, but we have been unable to derive an expression for $[\mathbf{2a}]_{\text{max},0} / [\mathbf{2a}]_{\text{max},Q}$ from the relevant rate equation for **2a** to help explain it. Our difficulties arise from the fact that the reaction that is quenched by added Q is a second-order process, and the product (i.e., **2a**) is reactive (with Q and/or itself) on the time scale of its formation. Nevertheless, kinetic simulations verify that $[\mathbf{2a}]_{\text{max},0} / [\mathbf{2a}]_{\text{max},Q}$ does indeed vary linearly with $[Q]$ over a range of 10^5 – $10^{10} \text{ M}^{-1}\text{s}^{-1}$ in k_Q , and indicate that an essentially perfect 1:1 correspondence between $K_{\text{SV}}^{\text{rel}}$ and k_Q^{rel} (see Figure 3) is obtained so long as the rate constant for germylene scavenging (k_Q) is more than ca. 10 times larger than that for scavenging of the dimerization product (k_Q^{2a}); a smaller difference between the reactivities of Ph_2Ge and **2a** toward a given reagent cause its $K_{\text{SV}}^{\text{rel}}$ -value to increase relative to k_Q^{rel} , by as much as a factor of ca. 2 when $k_Q = k_Q^{2a}$ (from ca. 1.1:1 when $k_Q = 10k_Q^{2a}$)

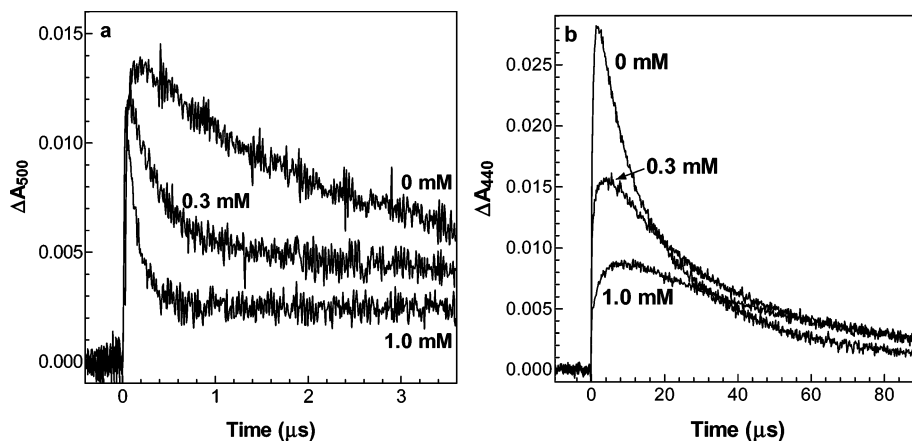


Figure 4. Effects of added isoprene on the transient absorptions due to (a) Ph_2Ge recorded at 500 nm and (b) **2a** recorded at 440 nm. Data recorded with isoprene concentrations of 0.6 and 2.0 mM were omitted for clarity.

so long as scavenging is irreversible (i.e., $k_Q/k_{-Q} > \text{ca. } 20,000 \text{ M}^{-1}\text{s}^{-1}$). In fact, all of the scavengers whose points lie to the right of the 1:1 correspondence line in Figure 3 are only 3–6 times less reactive toward **2a** than Ph_2Ge , so their positions in relation to the 1:1 line are more or less as expected. On the other hand, reversible scavenging (i.e., $k_Q/k_{-Q} < \text{ca. } 20,000 \text{ M}^{-1}\text{s}^{-1}$) results in highly variable behavior, depending on the specific details of the situation. The most dramatic effect occurs when the dimerization product is relatively unreactive toward the scavenger; in addition to other distinctive signs (vide infra), it results in smaller $K_{\text{SV}}^{\text{rel}}$ values than would be predicted based on the value of k_Q^{rel} . Most importantly, the exercise justifies the use of the relative Stern–Volmer constants to derive estimates of the absolute rate constants for scavenging by the less reactive reagents studied in this work, provided their reactions are irreversible, and indicates that we can do so with a level of precision that is not significantly less than that defined by the experimental errors in $k_{\text{Et}_3\text{N}}^{\text{rel}}$ and $K_{\text{SV}}^{\text{O}}/K_{\text{SV}}^{\text{Et}_3\text{N}}$.

With the primary and secondary amines (BuNH_2 and Et_2NH) and the alkyne (TBE), the behavior described above was accompanied by the formation of new transient absorptions at 270–330 nm, whose intensities increased with increasing reagent concentration until they became the only species detectable once the concentration reached moderate (ca. 2 mM) levels. With the amines, the new absorptions exhibit $\lambda_{\text{max}} = 310$ and 320 nm for BuNH_2 and Et_2NH , respectively, grow in with similar kinetics to the decay of the germylene under the same conditions, and then decay over several hundred microseconds with mixed-order kinetics. The species formed in the presence of TBE exhibits $\lambda_{\text{max}} = 275$ nm and decays with a lifetime $\tau \approx 0.5$ s. The spectra of these transient products are included in the Supporting Information.

As mentioned earlier, the behavior observed upon addition of Et_3N , isoprene, and DMP to solutions of **1a** was different from that observed with the other scavengers; one aspect of this is evident in the plot of $K_{\text{SV}}^{\text{rel}}$ vs k_Q^{rel} of Figure 3, where the points for these scavengers lie to the left of the 1:1 correspondence line while the others lie consistently to the right of it. Addition of these three reagents in concentrations of 0.1–3 mM caused acceleration of the germylene decay as before, but this was accompanied by a *lengthening* of the growth time of the digermene signal and much less efficient quenching of its maximum yield. As a result, decays recorded at 500 nm exhibited an initial fast component superimposed on a slowly

decaying residual absorption which is due only partially to digermene **2a**; furthermore, formation of the digermene could still be clearly detected at (higher) scavenger concentrations where the decay of the free germylene was too rapid to be resolved with our system. For example, Figure 4 shows representative growth/decay profiles recorded at 440 and 500 nm in the presence of various concentrations of isoprene over the 0.1–1.0 mM range. To correct for the underlying absorptions due to **2a**, growth/decay profiles were recorded at 440 nm on the same time scale for each isoprene concentration, and then subtracted from the 500 nm data after applying a scaling factor of 0.15, which was determined to be the optimum value of the relative extinction coefficients of **2a** at the two wavelengths in experiments using Et_3N as scavenger (vide infra). Figure 5a shows the 500 nm data of Figure 4a after scaled subtraction. Pseudo-first order decay rate constants for the initial rapidly decaying portions of the 0.3–2.0 mM data were then estimated by nonlinear least-squares fitting to single exponential decays (treating the residual absorptions as the “infinity” levels), and are shown plotted against isoprene concentration in Figure 5b; the slope of the plot is the approximate value of the rate constant for scavenging of Ph_2Ge by the diene: $k_Q = (5.5 \pm 1.2) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. The Figure also includes the Stern–Volmer plot obtained from the maximum digermene transient absorbances over the 0–2.0 mM range in isoprene concentration. Similar results (in every respect) were observed in the presence of 0.1–2.0 mM concentrations of DMP, and are reported in detail in the Supporting Information.

The behavior observed in the presence of Et_3N was somewhat different from that observed with isoprene and DMP, but still distinctly different from that exhibited by the other scavengers. First, the position of the maximum in the growth/decay curve with respect to the laser pulse did not change appreciably with increasing scavenger concentration; this is most likely due to the fact that the decay rate of the digermene was accelerated slightly in the presence of increasing concentrations of the amine. Second, correction of the 500 nm decay data as before (i.e., by subtraction of 15% of the intensity of corresponding traces recorded at 440 nm) yielded traces that decay with approximate first order kinetics completely to the pre-pulse level, and which show no hint of the long-lived residual absorptions that are present in the cases of isoprene and DMP. Absolute rate constants were obtained from linear least-squares analysis of the plots of k_{decay} vs $[\text{Q}]$ and are listed in Table 1, along

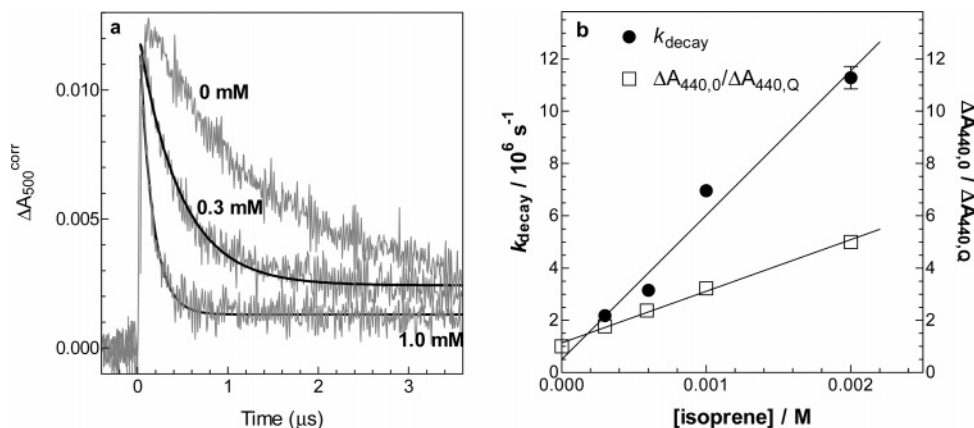


Figure 5. (a) Corrected germylene decay traces in the presence of isoprene, obtained by subtracting 15% of the intensities of the digermene signals at 440 nm (recorded on the same time scale) from the traces of Figure 4a; the solid lines represent the best nonlinear least-squares fit of the data to a single-exponential decay. (b) Plots of $\Delta A_{440,0}/\Delta A_{440,Q}$ vs [isoprene] (\square ; from the data of Figure 4b) and k_{decay} vs [isoprene] (\bullet), where the k_{decay} values are those obtained from the fits of the data of (a).

with the corresponding K_{SV} values obtained from plots of $(\Delta A_{440})_{\text{max},0}/(\Delta A_{440})_{\text{max},Q}$ vs $[Q]$.

Addition of these three reagents also resulted in the appearance of new transient absorptions at shorter wavelengths. In the case of Et_3N , the new transient exhibited $\lambda_{\text{max}} \approx 330$ nm and appeared as a shoulder on very strong transient absorptions ($\lambda_{\text{max}} < 290$ nm; $\tau \approx 2$ μs) due to competing photolysis of the amine. Nevertheless, measurements at 350 nm over the 0.3–1.0 mM concentration range revealed that the species grows in over the same time scale as Ph_2Ge decays; a plot of the growth rates vs $[\text{Et}_3\text{N}]$ was linear with a slope of $(6 \pm 1) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, in satisfactory agreement with the rate constant determined from the germylene decays. The species decays with mixed-order kinetics and an approximate lifetime of 100 μs , which appeared to decrease slightly with increasing amine concentration over the 0.3–2.0 mM range. Unfortunately, screening of the excitation light by the amine precluded experiments at higher concentrations.

In the presence of 0.3–3 mM concentrations of isoprene and DMP, the new species appeared simply as intensified transient absorptions in the 270–290 nm range. Continued addition of up to 50 mM of these reagents resulted in complete quenching of the germylene signal, further reductions in the yield of **2a**, and the eventual emergence of a single transient species absorbing at $\lambda_{\text{max}} = 285$ nm in the case of isoprene and $\lambda_{\text{max}} = 275$ nm in the case of the alkene. These new absorptions replaced the complex collection of absorptions that is observed in this range at low (or zero)³² scavenger concentrations, whose presence made it impossible to resolve a growth of the new species at lower concentrations. Figure 6 shows the transient absorption spectrum recorded from **1a** in the presence of 15 mM isoprene, which corresponds to the highest concentration at which a signal due to **2a** at 440 nm could be detected; the lifetime of the latter was $\tau \approx 275$ μs under these conditions, allowing an estimate of $k \approx 2.4 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ for the rate constant for reaction of **2a** with the diene. The figure also includes a representative decay trace for the new species at a diene concentration of 50 mM, where the decay follows clean first-order kinetics and exhibits a lifetime $\tau = 500 \pm 10$ μs .

The strength of the signal (and thus the concentration of the absorbing species) is significantly reduced at this concentration due to substantial screening of the excitation light by the diene,

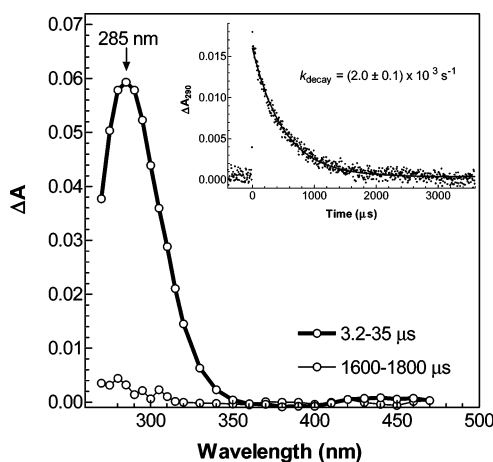


Figure 6. Transient absorption spectra from laser flash photolysis of a deoxygenated solution of **1a** in hexane containing 15 mM isoprene, recorded 3.2–3.5 μs and 1.6–1.8 ms after the pulse. The insert shows a decay trace recorded at 290 nm in the presence of 50 mM isoprene.

but this is useful because the lower transient concentration results in clean first-order decay kinetics. Analogous behavior was observed in the presence of 15–100 mM DMP, but in this case the new transient exhibited $\lambda_{\text{max}} = 275$ nm and a lifetime of $\tau = 1.2 \pm 0.1$ ms in the presence of 100 mM alkene. The spectrum and a representative decay trace for this species are included as Supporting Information.

Reactivity of Tetraphenyldigermene (2a). Most of the germylene scavengers studied in this work also caused discernible increases in the decay rate of digermene **2a**, within the concentration range where a signal for the digermene could be detected; the exceptions are Et_3SiH , CHCl_3 , and $\text{C}_5\text{H}_{11}\text{Br}$. The amines BuNH_2 and Et_2NH react by far the fastest, exhibiting absolute rate constants that are only a factor of 2–3 lower than those for reaction with Ph_2Ge ; in these cases absolute rate constants for reaction with the digermene could be obtained from the decay data at several concentrations of amine, as we reported previously for reaction with BuNH_2 .³² In most other cases, absolute rate constants could only be estimated from the digermene decays at the highest scavenger concentrations investigated, since the decays generally do not fit to perfect first-order kinetics at lower concentrations where oligomerization of the digermene competes with reaction with the scavenger. The data are collected in Table 2. The values reported for

Table 2. Absolute Rate Constants for Reaction of Tetraphenyldigermene (**2a**) with Various Reagents in Deoxygenated Hexane Solution at 23 ± 1 °C^a

reagent	$k_a^{2a}/10^6 \text{ M}^{-1}\text{s}^{-1}$	reagent	$k_a^{2a}/10^6 \text{ M}^{-1}\text{s}^{-1}$	reagent	$k_a^{2a}/10^6 \text{ M}^{-1}\text{s}^{-1}$
BuNH ₂	3640 ± 380 ^b	CCl ₄	2.0 ± 0.2	TBE	≤ 20 ± 2
Et ₂ NH	2400 ± 400	C ₂ Cl ₆	1.2 ± 0.1	DMP	≤ 5.1 ± 0.3
Et ₃ N	≤ 10 ± 2	Et ₃ GeH	5.6 ± 1.6	isoprene	≤ 0.3 ± 0.1
AcOH	≤ 20 ± 3 ^b	Bu ₃ SnH	410 ± 200	O ₂	4.8 ± 0.8

^a Measured by laser flash photolysis of ca. 0.003 M solutions of **1a**. Those reported as upper limits were determined from the digermene decay kinetics at the highest scavenger concentration employed, while the others were determined from plots of the digermene pseudo-first-order decay rate constants vs scavenger concentration. Errors are listed as ±2σ. ^b From ref 32.

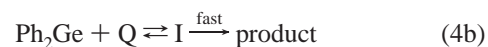
scavenging of **2a** by CCl₄ and O₂ are ca. 6 and 400 times slower, respectively, than those reported by Mochida and co-workers for tetramethyldigermene (**2c**), while that for scavenging by isoprene is similar to that reported for the **2c**/DMB system.³⁵ In contrast, the alkyne (TBE) reacts with **2a** at an upper limit of $k \approx 2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$, roughly 3 orders of magnitude faster than the reaction of **2c** with 1-hexyne.³⁵ To our knowledge, the reactions of digermenes with hydridogermanes and -stannanes has not been studied previously; our results indicate substantial reactivity, with the rate constant for reaction with the stannane exceeding that for the germane by a factor of ca. 100. Little mechanistic insight can be gleaned from the data at this point in time, as many of these reactions have not been widely studied and product studies are impractical without a source of the digermene that does not require dimerization of the significantly more reactive germylene. We thus defer more substantive comment on these data to a later publication.

Steady-State Trapping Experiments with C–C Unsaturated Compounds and Bu₃SnH. Steady-state photolysis experiments were carried out with deoxygenated solutions of **1a** (0.01–0.05 M) in C₆D₁₂ or hexane containing TBE, DMP or Bu₃SnH (0.01–0.05 M), irradiating the solutions with low-pressure mercury lamps (254 nm) and monitoring the photolyses over the 0–40% conversion range by ¹H NMR spectroscopy. The photolyses in the presence of the alkene and Bu₃SnH resulted only in the formation of polymeric material; in both cases, DMB could be detected in low steady state concentrations at conversions less than ca. 10%, but disappeared upon continued photolysis as broad absorptions in the aromatic and aliphatic regions of the NMR spectra grew in. On the other hand, the photolysis in the presence of TBE resulted in the formation of DMB with similar efficiency to that observed previously with other scavengers,³² and at least two other (as yet unidentified) products whose relative yields changed continuously with photolysis time. It can thus be concluded that while trapping of Ph₂Ge by the alkyne proceeds efficiently, the reaction affords a product that is sensitive to further thermal and/or photochemical reaction.

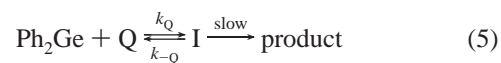
Discussion

The kinetic behavior observed with most of the scavengers studied in this work (all but isoprene, DMP, and Et₃N) is broadly consistent with *irreversible* reaction of the germylene with the scavenger to form a product that is indefinitely stable or at least relatively long-lived on the time scale of the experiment, as

would be formed in either a single-step concerted reaction (eq 4a) or a two-step reaction (eq 4b, where I is a steady-state intermediate) in which the second step is unimolecular and fast compared to reversion of I to the free reactants. The hallmarks of irreversible reaction appear in both the germylene decay and digermene growth/decay profiles, illustration of which is shown in Figure 1 for scavenging by Bu₃SnH, a typical irreversible scavenger. Decay of the germylene follows mixed pseudo-first and second-order kinetics at low [Q] due to competitive formation of digermene, but evolves into pure pseudo-first order kinetics as [Q] is increased to the point where dimerization is more or less completely suppressed. This behavior is accompanied by a decrease in the growth time of the digermene and hence a shift of its concentration maximum to shorter times after the laser pulse, which occurs because dimerization dominates the early part of the germylene decay where the concentration of the species is highest; formation of the digermene effectively stops once the concentration of free germylene is reduced to the point where pseudo-first-order reaction with the scavenger takes over. A lengthening of the decay of the digermene is also expected provided that it reacts at least ca. 10 times more slowly with the scavenger than the germylene does; this is because in the absence of a reactive scavenger, the decay of the digermene proceeds with second-order kinetics (due presumably to dimerization) and is hence dependent on the maximum concentration produced.



Much different behavior can be expected when the reversibly formed intermediate (I) of eq 4b is relatively long-lived, and builds up in appreciable concentration on the time scale of the experiment (eq 5). In this situation, dimerization takes place in two stages: an early stage that competes with the equilibration of the free germylene with Q to form the intermediate, and a slower one that involves dimerization of residual free germylene after equilibration is complete. As a result, the germylene decay shows an initial rapid component that reflects competing dimerization and pseudo-first-order approach to equilibrium with I, and a much slower-decaying residual absorption due to dimerization over the longer time scale; the amount of the residual absorption decreases and the initial decay accelerates as the concentration of Q is increased. In addition, the growth time of the digermene absorption *lengthens* as [Q] is increased. The maximum digermene concentration decreases with increasing [Q], but the Stern–Volmer constant (K_{SV}) will be smaller than what would be expected based on the value of k_Q estimated from the germylene decays. The behavior observed of the digermene signals in the presence of Et₃N, isoprene (Figures 5 and 6), and DMP are consistent with this situation.



It should be stressed that the behavior of the digermene absorbance vs time profiles described above for the situation of eq 5 represents a limiting situation in which the equilibrium constant for the formation of I is less than ca. 20 000 M⁻¹ and the digermene is at least an order of magnitude less reactive

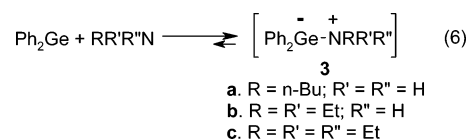
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than the germylene toward the scavenger. In fact, the latter condition is met by only a few of the scavengers studied in the present work, most notably isoprene, DMP, and Et₃N. All of the others appear to react with **2a** on the order of only 3–10 times more slowly than with Ph₂Ge. Between this, the fact that the signals are relatively weak, and the significant degree of spectral overlap between the germylene and digermene absorptions, a considerable degree of caution is advisable in interpreting the qualitative features of the digermene growth/decay profiles as indicative of irreversible reaction of the germylene, particularly for those scavengers that react relatively rapidly with **2a** (such as BuNH₂ and Et₂NH in particular). The only scavenger that we can definitively classify as truly “irreversible” on the basis of its effects on the germylene decay and digermene growth/decay profiles is AcOH, which reacts with **2a** at least 200 times more slowly than with Ph₂Ge.³² With the exception of the amines, isoprene and DMP, the most definitive statement that we can make for the others is that the equilibrium constant for the primary scavenging reaction is in excess of ca. 20 000 M⁻¹.

Lewis Acid–Base Complexation with 1°, 2°, and 3° Amines. The overall course of the reactions of Ph₂Ge with BuNH₂ and Et₂NH is not completely understood; product studies with BuNH₂ indicate that it yields mainly oligo- or polymeric material, accompanied by extremely small amounts of a product tentatively assignable to the simple N–H insertion product on the basis of NMR evidence.³² While N–H insertion reactions with amines have not been widely documented, to our knowledge,^{5,36,37} the complexation of reactive germylenes with tertiary amines and other Lewis bases is well-known,^{5,29,38–41} and has been shown to be synthetically useful for its ability to suppress oligomerization processes and allow preparative reactions involving transient germylenes (e.g., Me₂Ge^{39–41}) to proceed relatively cleanly. More recently, several examples of isolable germylenes stabilized by intramolecular coordination to a remote amine functionality have been reported.^{42,43} The present paper represents the first instance in which the kinetic details of the primary association process have been examined directly for a transient germylene derivative.

The results indicate that the reactions of Ph₂Ge with BuNH₂ and Et₂NH proceed at close to the diffusion controlled rate, and thus show only small variations in rate with the degree and type of alkyl-substitution on the amine. Similarly, the nearly identical rate constants for reaction of BuNH₂ with Me₂Ge and Ph₂Ge³² indicates there to be little dependence on electronic or steric substituent effects in the germylene, at least with primary amines. With Ph₂Ge, the observation of new transient absorptions below 350 nm, that increase in intensity with increasing amine concentration and are formed in concert with decay of the germylene, lead us to conclude that the primary products of the reactions are the Lewis acid–base complexes **3** (eq 6).

The spectra of these species (see Supporting Information) are similar to those reported by Ando and co-workers for Ph₂Ge in 3-methylpentane matrixes containing quinuclidine at 77K (λ_{\max} = 334 nm).^{29,38} The reactions of BuNH₂ and Et₂NH with Ph₂Ge appear to be effectively irreversible, based on the qualitative indications afforded by the germylene and digermene transient absorption profiles, which are similar to those shown in Figure 1 for scavenging by Bu₃SnH. As noted above, however, the secondary reactions of **2a** with these two amines are only a factor of 2–3 times slower than with Ph₂Ge, which could very well mask the effects of reversibility on the growth/decay kinetics of the digermene. Nevertheless, the fact that the germylene decays with clean first-order kinetics completely to the pre-pulse level at sub-millimolar amine concentrations indicates that the equilibrium constant must be in excess of ca. 2×10^4 M⁻¹, which is the approximate upper limit at which we would be able to detect the effects of reversibility on the germylene decay profiles. The tertiary amine (Et₃N), on the other hand, is more than 200 times less reactive with **2a** than with Ph₂Ge, and hence the behavior of the digermene signals in the presence of this reagent exhibits the distinctive signs of reversible scavenging of the germylene. Furthermore, the K_{SV} value is significantly lower than would be expected from the value of k_Q , resulting from the fact that formation of the digermene persists even at high enough amine concentrations to reduce the concentration of free germylene to undetectable levels. The behavior of the germylene absorptions indicates that the equilibrium constant for complexation with the tertiary amine is still in excess of ca. 2×10^4 M⁻¹, and hence greater than we can measure by the present methods. In the presence of up to ca. 2 mM Et₃N, the highest concentration that can be employed in our experiments due to complications from short-wavelength transients that originate from photolysis of the amine, the complex is quite long-lived ($\tau \approx 100$ μ s) but is certainly not indefinitely stable.



The observation of these species as discrete, long-lived intermediates in the reaction of Ph₂Ge with the primary and secondary amines indicates that unimolecular [1,2]-H migration within the complex, to yield the formal N–H insertion product, is relatively slow. Indeed, the complexes formed between Ph₂Ge and Et₂NH and BuNH₂ decay with good second-order kinetics in the presence of sub-millimolar concentrations of amine and exhibit lifetimes in excess of ca. 50 μ s, which indicates that catalyzed decomposition involving a second molecule of amine (for example, by initial deprotonation) is relatively slow as well, at least at millimolar concentrations of free amine and below. Because competing light absorption at 248 nm by the amines precludes experiments at higher concentrations, we cannot comment more precisely on the likely true mode of decay of these species that would apply at high amine concentrations; at the low concentrations that our experiments are limited to, it may well be that the decay is dominated by dimerization of the free germylene, present at very low concentrations in equilibrium with the complexes.

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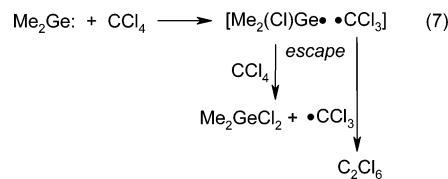
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Scavenging by Halocarbons and Oxygen. CCl_4 and O_2 have been used extensively as scavengers in previously reported time-resolved studies of germynes in solution.^{34,44–47} This includes Ph_2Ge , for which rate constants for scavenging by CCl_4 vary over the range $1.5\text{--}2.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$,^{34,46,47} a factor of at least 10 higher than the value of $1.1 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ reported in the present work. Our estimated rate constant for reaction with oxygen ($k_{\text{O}_2} \approx 3 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$) is also significantly lower than reported values, which range from $1\text{--}3 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ ^{44,45} to as high as $7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$.⁴⁷ On the other hand, the present rate constants for reaction of O_2 and CCl_4 with Ph_2Ge are both ca. 4 times larger than the corresponding rate constants for reaction with Me_2Ge ,³¹ whose assignment can be considered secure. Furthermore, a value of $k_{\text{O}_2} = 4.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ has been reported for Me_2Ge in the gas phase;²³ this corresponds to a solution phase value of $2.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$, which is similar to the value reported here for Ph_2Ge in solution.

The reaction of germynes with O_2 is thought to yield the corresponding germanone (which goes on to react further; see Scheme 1),^{5,48,49} but the mechanistic details of the process have evidently not been studied. The reaction is presumably analogous to that of silylenes, for which it is known that the initially formed product is a dioxasilirane, formed presumably by collapse of the triplet 1,3-biradical resulting from addition of (triplet) oxygen to the silylene.^{50–52} It is interesting to note that the rate constants reported here for Ph_2Ge and earlier for Me_2Ge ($k_{\text{O}_2} = 7.3 \times 10^6$)³¹ are quite similar to the value of $3.2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ reported by Conlin and co-workers for reaction of O_2 with dimethylsilylene in cyclohexane at ambient temperatures,⁵³ but are roughly 100 times slower than that for dimethylsilylene under similar conditions.⁵⁴

The reaction of germynes with halocarbons has been much more extensively investigated, in particular with Me_2Ge .^{55–58} The products and CIDNP effects observed upon reaction of Me_2Ge with benzyl halides, CCl_4 , and bromotrichloromethane are consistent with the initial formation of a singlet radical pair via formal halogen atom abstraction, the fate of which varies between predominant cage recombination in the case of benzyl bromide and cage escape in the cases of CCl_4 and bromotrichloromethane.^{56–58} With CCl_4 , for example, the major products are Me_2GeCl_2 and hexachloroethane, formed by the mechanism shown in eq 7.^{56,58} The analogous dichlorogermane (Ph_2GeCl_2)

is also the major product of reaction of Ph_2Ge with this halocarbon.³⁴



While a general trend toward increasing efficiency with decreasing C–X bond dissociation energy has been noted previously in the trapping of Me_2Ge by halocarbons,⁵⁸ it is clear that the precise course of the reaction varies with the halocarbon; for example, CIDNP effects are not observed in the reaction of Me_2Ge with allyl and vinyl halides, which has led to the suggestion of a concerted mechanism in these cases.^{5,56} In the case of Ph_2Ge , the rate constants for reaction with CCl_4 ($1.1 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$), C_2Cl_6 ($4.1 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$), $\text{C}_5\text{H}_{11}\text{Br}$ ($\sim 4.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$) and CHCl_3 ($\sim 2 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$) do not correlate with the calculated C–X bond dissociation energies nor the (aqueous) one-electron reduction potentials of these compounds.⁵⁹ Further work is necessary in order to develop a more comprehensive picture of the mechanisms of the reactions of germynes with compounds of this type.

M–H Insertion Reactions with Group 14 Hydrides. The kinetic results for the reactions of Ph_2Ge with Et_3SiH , Et_3GeH , and Bu_3SnH suggest that scavenging is in each case formally irreversible, proceeding with rate constants that correlate with M–H bond strength.^{60,61} $k_{\text{SnH}} \approx 120k_{\text{GeH}} \approx 6000k_{\text{SiH}}$. The rate constant estimated in the present work for reaction of Ph_2Ge with Et_3SiH ($k_{\text{Q}} \approx 6 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$) corrects the 100-fold lower value reported earlier by other workers,⁴⁴ and is only ca. 5 times higher than the corresponding rate constant for Me_2Ge .³¹ The present data for reaction of Ph_2Ge with Et_3SiH and Et_3GeH can be compared to the results of the gas-phase kinetic studies of Walsh and co-workers on H_2Ge , which show that the parent molecule reacts with germane (GeH_4) and Et_3GeH with rate constants 3–4 times greater than with silane (SiH_4) and Me_3SiH , respectively.^{11,12,14,62} Considering that the rate constant for reaction of H_2Ge with Et_3GeH is within a factor of 2 of the collisional rate under the conditions studied⁶² while the solution phase rate constant for reaction of Ph_2Ge with the same reagent is ca. 10^3 times slower than the diffusional limit, the relative reactivities of the two species toward Si–H and Ge–H bond insertion compare reasonably well. Unfortunately, for Me_2Ge only upper limits of ca. 5×10^{-15} and ca. $4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (corresponding to solution phase values of ca. 3×10^6 and $2.4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, respectively) could be estimated for the gas-phase reactions with Me_3SiH and Me_3GeH , respectively.^{23,62} These upper limits are nevertheless consistent with the absolute rate constants reported here for reaction of Ph_2Ge with Et_3SiH and Et_3GeH .

The mechanism of the Ge–H insertion reaction has been proposed to involve initial (reversible) formation of an H-bonded complex between the gerylene and the germane, consistent

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with the fact that the reactions of both GeH_4 and Et_3GeH with H_2Ge exhibit negative activation energies.^{11,62} Ab initio calculations suggest that bonding in the complex involves the empty 4p-orbital on the germylene with accompanying transfer of negative charge to this site;^{11,63} the reaction can thus be broadly viewed as beginning as a hydride transfer, the course of which is interrupted by attack of the germylene lone pair on the second germanium to form the Ge–Ge bond of the final (digermene) product in the rate-determining step (eq 6). A similar mechanism has been proposed for the reaction of H_2Ge with SiH_4 , again on the basis of high level ab initio calculations,¹⁴ and the slightly smaller rate constant and less negative activation energy relative to those for reaction with GeH_4 explained in terms of relative M–H bond strengths. Interestingly, Mochida and co-workers reported a Hammett ρ -value of +1.04 for the reaction of Me_2Ge with a series of aryltrimethylsilanes in benzene solution at 70 °C, where relative rate constants were measured by competition methods.⁶⁴ A mechanism involving a pentacoordinate, zwitterionic intermediate (with negative charge at silicon) was proposed in explanation, but the results also appear to be consistent with the mechanism of eq 8, in which nucleophilic attack by the germylene lone pair occurs in the rate determining step for reaction.

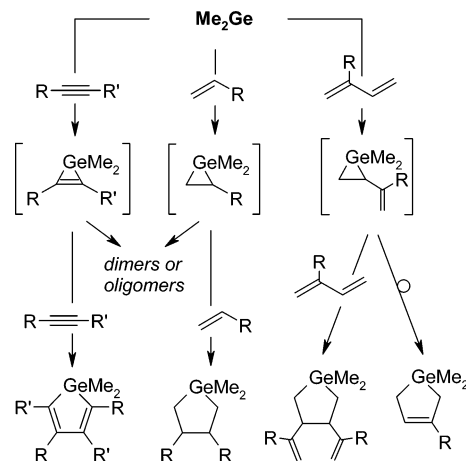


To our knowledge, there are no studies reported of the reactions of germynes with tin hydrides, though examples exist of insertions into Sn–C⁶⁵ and Sn–halogen^{57,58} bonds. The latter are not true insertions, however, proceeding via a halogen atom-abstraction mechanism similar to that involved in the reaction with halocarbons (vide supra).⁵⁷ Our preliminary attempts to identify the primary product(s) of the reaction of Bu_3SnH with Ph_2Ge have been so far unsuccessful; under the conditions of our steady state photolysis experiments, only intractable polymeric material is formed. We thus cannot yet comment on the course of the primary reaction in this case; the results are consistent with either concerted Sn–H insertion, the anticipated product of which can be expected to possess pronounced photolability,⁶⁶ or a nonconcerted pathway involving germanium- or tin-centered radicals. We see no evidence for the formation of such species by laser flash photolysis, however.

Reaction with Alkenes, Alkynes, and Conjugated Dienes.

Our flash photolysis results indicate that Ph_2Ge reacts rapidly with the C–C unsaturated bonds in *tert*-butylacetylene (TBE), 4,4-dimethyl-1-pentene (DMP), and isoprene, with absolute rate constants on the order of $(4\text{--}6) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. These also compare quite favorably with absolute rate constants reported for the reaction of Me_2Ge with related molecules in the gas phase.²³ For example, reaction with acetylene and 1,3-butadiene proceed with pressure independent rate constants of $1.1\text{--}1.3 \times 10^{11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$, corresponding to solution phase values of $6.6\text{--}7.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, while reaction with ethylene is pressure dependent and proceeds with $k = 6.9 \times 10^{12}$

Scheme 2



$\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ ($\sim 4.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) at 100 Torr.²³ The parent molecule (H_2Ge) exhibits substantially greater reactivity toward acetylene, ethylene, and propene, for which the rate constants approach to within 0.5–0.7 of the collisional limit.^{9,10,15,16,19,21,22} The reactions of H_2Ge with acetylene²¹ and ethylene^{16,22,67,68} have been explored in detail by high level theoretical methods.⁶⁸ In each case, the primary products of these reactions are thought to be the corresponding three-membered ring compounds (germirene and germirane, respectively), which are themselves highly reactive toward further unimolecular rearrangement processes. The reactions of Me_2Ge with C–C multiple bonds in solution has been extensively studied,^{4,5,69,70} and is also thought to proceed via the initial formation of the corresponding three-membered germanocycle, which is prone to further reaction with a second molecule of substrate (to yield five-membered ring compounds) or by dimerization (see Scheme 2). Reaction of Me_2Ge with aliphatic dienes cleanly affords the corresponding germacyclopent-3-ene in the gas phase at high temperatures,^{71,72} but in solution at ca. 70 °C, the intermediate vinylgermirane undergoes competing addition of a second molecule of diene.⁶⁹ The relatively low kinetic stability of these compounds is well-known, and only a few examples of sterically stabilized germirene^{73–76} and germirane⁷⁵ derivatives have been reported.

The present results indicate that the reaction of Ph_2Ge with the alkyne (TBE) proceeds effectively irreversibly, while those with the alkene (DMP) and isoprene proceed reversibly under the conditions of our experiments. The indications of reversibility in the latter two reactions are quite distinctive, and appear in the absorbance vs time profiles of both the germylene and the digermene over the 0.3–2.0 mM concentration range of added substrate (see Figures 4 and 5). The germylene decays show quite clearly that despite rapid quenching, significant

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amounts of free germylene remain behind after the initial scavenging process is “complete”, resulting in continued formation of digermene over a prolonged time scale. As with Et_3N , this results in smaller Stern–Volmer constants than the absolute k_Q -values would predict, based on the (1.4–1.8):1 correlation between K_{SV} and k_Q that is observed for all the other scavengers studied in this work.

From the initial and residual transient absorbance values for the germylene as a function of scavenger concentration, it is possible to estimate the equilibrium constants (K_{eq}) for formation of the initial products of reaction with isoprene and DMP from the relation of eq 9, where $\Delta A_{500,0}$ and $\Delta A_{500,\text{res}}$ are the (corrected) initial and residual absorbances due to Ph_2Ge at 500 nm in the presence of the scavenger at concentration $[\text{Q}]$. This assumes a 1:1 correspondence between the amounts of free germylene lost and product formed in the reversible process, and treats the residual absorption as nondecaying. The latter is, in fact, approximately true on the time scale of the measurements for substrate concentrations higher than 0.5 mM, as the data of Figure 5a show. Using the best-fit values of the initial and residual transient absorbances from the nonlinear analyses of the decays of Figure 5a for $[\text{isoprene}] = 0.3\text{--}2.0$ mM, we obtain a value of $K_{\text{eq}} = 6000 \pm 2500 \text{ M}^{-1}$ from a plot according to eq 9 (see Supporting Information), corresponding to a free energy difference of $\Delta G = -5.1 \pm 0.3 \text{ kcal mol}^{-1}$. A similar calculation from the data obtained for DMP leads to $K_{\text{eq}} = 2500 \pm 600 \text{ M}^{-1}$ and a free energy difference of $\Delta G = -4.6 \pm 0.2 \text{ kcal mol}^{-1}$; the complete data workup for the experiments with the alkene are provided in the Supporting Information.

$$K_{\text{eq}}[\text{Q}] \approx (\Delta A_{500,0} - \Delta A_{500,\text{res}})/(\Delta A_{500,\text{res}}) \quad (9)$$

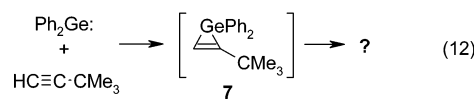
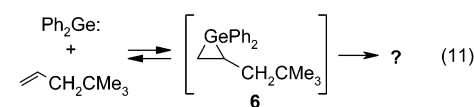
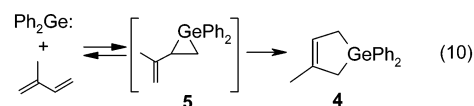
Kinetic simulations have been employed to verify the validity of the data analysis employed for the results for isoprene and DMP, using similar values for the rate and equilibrium constants to those determined above and rate constants of $2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ for the di- and oligomerization of Ph_2Ge and **2a**, respectively. The rate constant for dimerization of the germylene is a factor of ca. 2 higher than the value estimated by us previously,³² but is required (as is the value employed for the oligomerization of **2a**) in order to reproduce the time scale of the digermene decay/growth profiles reasonably faithfully; we consider the difference to be well within the limits of accuracy of our previous determination. The simulations (see Supporting Information) afford germylene decay and digermene growth/decay profiles that are qualitatively very similar to the actual data obtained for isoprene and DMP over the 0.3–2.0 mM concentration range; furthermore, secondary analysis of the simulated data in the same manner as employed for the real data returns values for k_Q and K_{eq} that are within 5% of the input values. We thus conclude that the methods employed to extract the rate and equilibrium constants from the data, as crude as they may seem considering that the germylene decays proceed with mixed first- and second-order kinetics, provide quite good approximations to the actual situation.

As with the amines, addition of the three C–C unsaturated compounds results in the formation of new, long-lived transient absorptions at shorter wavelengths, centered at $\lambda_{\text{max}} = 285$ nm in the case of isoprene (see Figure 6), and $\lambda_{\text{max}} \sim 275$ nm in the cases of DMP and TBE. These are the only species detectable at “high” scavenger concentrations, which correspond

to >3 mM in the case of TBE and >15 mM with isoprene and DMP, and we identify them as the initial products of the reactions of Ph_2Ge with these reagents. The species obtained from isoprene and DMP decay with mixed order kinetics under the usual conditions of our experiments, but this converges to good first-order kinetics at reduced laser intensities; that formed by reaction of Ph_2Ge with isoprene exhibits $\tau = 500 \pm 10 \mu\text{s}$, while that from DMP exhibits $\tau = 1.2 \pm 0.1$ ms. The species formed from TBE is much longer-lived, decaying with reasonably clean first-order kinetics and $\tau \sim 600$ ms at a substrate concentration of 2.5 mM. These lifetimes presumably reflect the rate constants for further unimolecular reaction of the three species.

In the case of the diene, the final product formed (under conditions of low light intensity) is the 1-germacyclopentene derivative **4** (see Scheme 1);^{24,33} this is true even in the presence of as much as 0.5 M of the diene,³² so it is clear that further reaction of the initially formed transient species occurs strictly by a unimolecular pathway, leading presumably to this compound. Product studies with the alkene (DMP) indicate that the species formed in this reaction does not lead to the formation of a tractable product under conditions of photochemical generation, but rather to polymerization, which consumes even the diene that is formed along with Ph_2Ge in the primary photoprocess. The situation is less clear with TBE; our preliminary experiments (see Supporting Information) indicate that a single major product is formed in the early stages of the photolysis, but this is converted to one or more additional products upon continued irradiation. These uncertainties aside, our flash photolysis results suggest that the initially formed intermediate in the reaction of Ph_2Ge with DMP undergoes subsequent unimolecular reaction with a rate constant only ca. twice smaller than that of the intermediate detected in the reaction with isoprene; it is presumably this process that is responsible for the formation of polymeric material in the steady state experiment. The intermediate formed from TBE is considerably more stable, undergoing further reaction with a first-order rate constant some 3 orders of magnitude lower than this.

While definitive assignments of the structures of the three intermediates cannot be made on the basis of the data currently at hand, the most obvious candidates are the three-membered germanocycles **5–7** (eqs 10–12); a seemingly less likely possibility is π -complexes that could precede the formation of these reactive molecules in some or all cases. The latter species, which can be viewed in the same context as the Lewis acid–base complexes formed by germylens with heteroatom donors, have been implicated in recent theoretical calculations on the



reactions of ethylene with H_2Ge ^{16,67,68} and Me_2Ge ,⁶⁸ where they exist as (very) shallow minima on the potential energy surfaces for germirane formation. More recent calculations on the reaction of H_2Ge with acetylene indicate that the formation of germirene is 3.2 kcal mol⁻¹ more exothermic than that of germirane from $\text{H}_2\text{Ge} + \text{ethylene}$ ¹⁶ at the G2//QCISD/6-31-G(d) level of theory, but find no evidence for the involvement of a π -complex in this reaction.²¹ With entropic factors included, the calculations suggest that formation of germirane from $\text{H}_2\text{Ge} + \text{ethylene}$ is exergonic by at most a few kcal mol⁻¹,^{16,67,68} while the analogous formation of germirene is slightly more so.²¹

In the end, the comparison to theoretical results for the smaller systems seems to favor a germirene (**7**) assignment for the species formed in the reaction of Ph_2Ge with TBE; it is formed effectively irreversibly and undergoes subsequent reaction relatively slowly, presumably initiated via (unimolecular) ring opening ($k \approx 2 \text{ s}^{-1}$). The situation is somewhat less clear for the species detected as primary products in the reactions with the alkene (DMP) and diene (isoprene), though we favor the germirane and vinylgermirane assignment, respectively, on the basis of the differences in UV absorption maxima and lifetimes of the two species. The calculations discussed above lead to the expectation that germirane (**5** and **6**) formation should be somewhat less exergonic than the formation of **7** from TBE, which is consistent with the fact that the former are reversible while the latter is not. Further work is required in order to establish the identity of these species conclusively, and to elaborate on their chemical and spectroscopic behavior. Clearly, the kinetics of the reactions of germynes with alkenes and dienes can be expected to be exquisitely sensitive to temperature and substituent effects (on both the germylene and the substrate), and a great deal remains to be learned from further study of these reactions.

Summary and Conclusions

Diphenylgermylene (Ph_2Ge) is a highly reactive, ground state singlet species whose direct detection in solution by time-resolved UV/vis spectroscopy requires generation in sufficiently high concentrations that dimerization to the corresponding digermene (**2a**) is difficult to avoid. The digermene is formed at or very close to the diffusion-controlled rate in hexane at 23 °C, and its absorption spectrum overlaps strongly with the significantly weaker spectrum due to the germylene at longer wavelengths. Despite the complexities this introduces in the kinetic behavior of the germylene in the presence of scavengers, it provides a useful qualitative probe of several important details of the scavenging reaction, including its general efficiency and whether it proceeds reversibly. With our experimental setup, the observation of good first-order kinetics in the germylene decays requires the presence of sufficient scavenger to reduce its lifetime to less than 1 μs , when the scavenging reaction is "irreversible" (i.e., $K_{\text{eq}} > \text{ca. } 2 \times 10^4 \text{ M}^{-1}$). Within more stringent limits, absolute rate constants for reactions of the digermene can also be determined; in general however, doing so accurately requires that scavenging of the digermene proceed with a rate constant that is no more than a factor of 3–5 lower than the corresponding reaction with its (germylene) precursor. This is in fact rarely the case, but in most instances it is at least possible to estimate a reasonable upper limit of the rate constant for reaction of the digermene.

A number of common germylene reactions have been studied quantitatively in this work, including Lewis acid–base complexation with amines, Group 14 M–H bond insertions, and reaction with halocarbons, oxygen, and aliphatic alkynes, alkenes, and dienes. The kinetics of a number of these reactions have been studied previously in the gas phase with the simpler germynes H_2Ge and Me_2Ge . Where overlap with existing data exists, the results reported here for Ph_2Ge in hexane solution correlate across the board with those reported previously for the gas-phase reactions of Me_2Ge with the same or similar substrates, and in many cases provide additional information that would be much more difficult to unravel in gas-phase experiments.

The most information-rich systems that we have studied in the present work are the reactions of Ph_2Ge with C–C unsaturated compounds. These reactions are generally thought to proceed via the initial formation of the corresponding three-membered germanocycles, which we believe we have detected in our experiments, albeit with some reservation at the moment. With the specific substrates we have examined in this work, the reactions with alkene and diene proceed reversibly while that with the alkyne is irreversible; this feature and the relative lifetimes measured for these species are in good agreement with what is known of the relative stabilities of such compounds from gas-phase experiments and theoretical calculations on smaller molecules, as well as the numerous attempts by others to synthesize stable analogues.

Further work on the kinetic and thermodynamic details of several of these and other reactions of diaryl-, alkylaryl-, and dialkylgermylenes in solution is in progress in our laboratory.

Experimental Section

Compound **1a** was synthesized as described previously.³² Hexanes (EMD Omnisolv) for laser flash photolysis experiments was dried by refluxing for several days under argon over sodium/potassium amalgam followed by distillation. 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 , triethylgermane (Et_3GeH), and tri-*n*-butylstannane (Bu_3SnH) were stirred at room temperature for 18 h over lithium aluminum hydride and distilled under mild vacuum. CCl_4 was refluxed over phosphorus pentoxide and distilled. Chloroform, hexachloroethane (C_2Cl_6), and 4,4-dimethyl-1-pentene (DMP) were dried by passage through a silica gel column, while isoprene, 3,3-dimethyl-1-butyne (TBE), and 1-bromopentane were distilled at atmospheric pressure.

Laser flash photolysis experiments employed the pulses from a Lambda Physik Compex 120 excimer laser filled with $\text{F}_2/\text{Kr}/\text{Ne}$ mixtures (248 nm; $\sim 25 \text{ ns}$; $100 \pm 5 \text{ mJ}$), and a Luzchem Research mLFP-111 laser flash photolysis system, modified as described previously.³² Solutions were prepared at concentrations such that the absorbance at the excitation wavelength was between ca. 0.7 and 0.9, and were flowed continuously through a thermostated $7 \times 7 \text{ mm}$ Suprasil flow cell connected to a calibrated 100 mL reservoir, fitted with a glass frit to allow bubbling of argon gas through the solution for at least 30 min prior to and then throughout the duration of each experiment; the entire apparatus was dried in a vacuum oven at 65–85 °C before use. Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple inserted directly into the flow cell. Reagents were added directly to the reservoir by microliter syringe as aliquots of standard solutions. In experiments with those scavengers that absorb at the laser wavelength, the concentrations employed were kept low enough to ensure that the fraction of the excitation light

absorbed by the scavenger never exceeded ca. 10%, to avoid complications in the kinetics due to screening effects or the formation of potentially reactive species from co-photolysis of the scavenger. For experiments using oxygen as scavenger, solutions of selected O₂/N₂ ratios were prepared by adding the appropriate volume of a nitrogen-saturated solution of **1a** in hexane to an oxygen-saturated hexane solution of the same concentration in **1a**.

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. Rate constants were calculated by linear least-squares analysis of decay rate-concentration data (generally 4–7 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.

Kinetic simulations were carried out using KinTekSim version 3.0.3 (KinTek Corp.).⁷⁷

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Supporting Information Available: Transient absorption spectra and decay profiles of Ph₂Ge-amine complexes and the transient products of reaction of Ph₂Ge with DMP and TBE, decay/growth profiles for Ph₂Ge and **2a** in the presence of 0–3 mM DMP and resulting quenching plots, details of kinetic simulations, and NMR spectra showing the results of photolysis of **1a** with DMP and TBE. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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