Nanosecond Laser Flash Photolysis Studies of the Photochemistry of Dimesitylgermylene Precursors

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The absolute rate constants for quenching of the transient absorption assigned to dimesitylgermylene with oxygen, triethylsilane, ethanol, and 1-bromohexane have been determined by nanosecond laser flash photolysis to be $(7.3 \pm 0.8) \times 10^6$, $(1.1 \pm 0.1) \times 10^5$, $<10^3$, and $(5.4 \pm 0.5) \times 10^5$ M^{-1} s^{-1}, respectively. The rate constants are compared to those obtained for the quenching of dimethyl- and diphenylgermylene and dimesitylsilylene.

Introduction

To date, the only successful route to relatively stable derivatives of germasilenes ($R_2Si=GeMes_2$) has been the regioselective thermolysis[1] or photolysis[2,3] of siladigermiranes:

$$Mes_2Ge: \quad + \quad Mes_2Ge=SiR_2 \qquad (1)$$

R = Mes, *t*-Bu
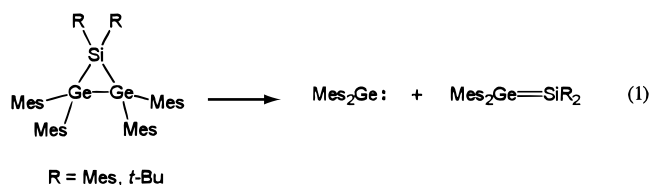
The cleavage reactions of these three-membered-ring compounds also produce dimesitylgermylene (Mes_2Ge; mesityl = 2,4,6-trimethylphenyl), for which we have obtained indirect evidence by trapping reactions with methanol,[1] triethylsilane,[2,4] 2,3-dimethylbutadiene,[5] and benzaldehyde.[6] Mes_2Ge has also been generated by Ando and co-workers by the photolysis of dimesitylbis-(trimethylsilyl)germane and characterized by UV−vis spectroscopy in a matrix.[7–9] The fate of this intermediate, in the absence of traps, is generally accepted to be dimerization to the well-known tetramesityldigermene ($Mes_2Ge=GeMes_2$).[7–9] The dimerization of germylenes to digermenes is one of the most important routes to the doubly bonded species.[10]

Germylenes, both reactive and stable, have long played a central role in the chemistry of germanium compounds and continue to be of considerable interest.[11] Considering the importance of diorganogermylenes, there is surprisingly little kinetic data available char-acterizing the reactions of these compounds. Gaspar and co-workers have investigated the kinetic spectroscopy of diphenylgermylene[12] and dimethylgermylene.[13] Mochida and co-workers have carried out extensive studies on the kinetics of quenching reactions of germylenes (for example, R_2Ge: R = Me, Et, Bu, Hex, Ph, PhMeGe) from a variety of precursors.[14] Despite the accumulated data, there continue to be discrepancies between the rate constants obtained.[13]

In view of our interest in the reactivity of Mes_2Ge, and the interest in the kinetics of germylene reactions, we have determined the rate constants for reaction of dimesitylgermylene, photochemically generated from dimesitylbis(trimethylsilyl)germane[7] and/or hexamesitylcyclotrigermane,[15] with some commonly used trapping reagents in solution at room temperature. Our results will be compared to the kinetic data for germylene reactions and the related Mes_2Si[16] already available in the literature.

Results

Nanosecond laser flash photolysis (NLFP) of a continuously flowing, deoxygenated solution of dimesitylbis-(trimethylsilyl)germane (**1**; ca. 1.5×10^{-4} M) in hexane with the pulses (248 nm, 80−120 mJ, 16 ns) from a Kr/

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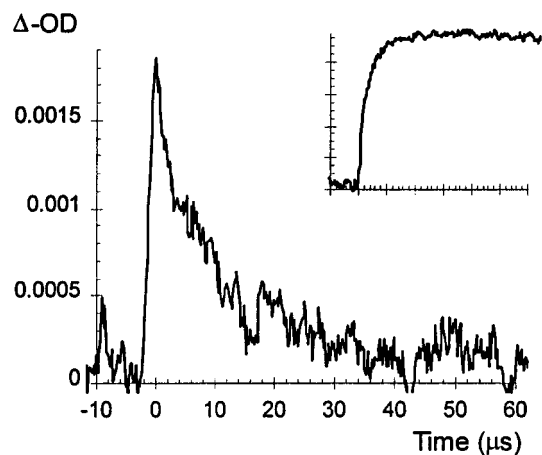
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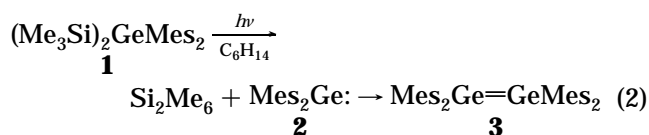
Figure 1. Transient decay trace, from nanosecond laser flash photolysis of a deoxygenated, ca. 1.5×10^{-4} M solution of **1** in hexane at 23 °C, recorded at a monitoring wavelength of 550 nm. Insert: growth trace monitored at 405 nm.

F_2 excimer laser resulted in the production of readily detectable transient absorptions, whose temporal characteristics and intensities varied considerably as a function of monitoring wavelength. Very weak signals, which appear to decay over several hundred microseconds with predominantly second-order kinetics, were observed at monitoring wavelengths in the 500−600 nm range (Figure 1). This is in contrast with the behavior at monitoring wavelengths in the 400 nm range, where a reasonably strong signal was observed to grow over a similar time scale, with second-order kinetics, to a residual level which decayed only slightly over the maximum time range of our system (5 ms). Transient UV absorption spectra were recorded for the solution in point-by-point fashion throughout selectable time windows after the laser pulse and are shown in Figure 2. Figure 2a shows the spectrum of species present "immediately" (*i.e.*, 0−2 μs) after excitation, while Figure 2b shows the spectrum of species present 50−60 μs after excitation (at the very end of the time window represented in Figure 1).

The UV spectrum of the weak transient observed from flash photolysis of the bis(silyl)germane **1** shows distinct bands centered at ∼550 and ∼325 nm, and is consistent with dimesitylgermylene (**2**; eq 2). The spectrum is

$$(Me_3Si)_2GeMes_2 \xrightarrow[C_6H_{14}]{h\nu}$$
$$\mathbf{1}$$
$$Si_2Me_6 + Mes_2Ge: \rightarrow Mes_2Ge{=}GeMes_2 \quad (2)$$
$$\qquad\qquad \mathbf{2} \qquad\qquad\qquad \mathbf{3}$$

similar to that reported by Ando and co-workers from photolysis of **1** in a hydrocarbon matrix at 77 K and assigned to this species.[7−9] The species with λ_{max} ∼405 nm, whose second-order growth is similar to the decay of **2**, can be assigned to the known[7−9] tetramesityldigermene (**3**).

Similar experiments with deoxygenated ca. 4×10^{-5} M hexane solutions of hexamesitylcyclotrigermane (**4**) afforded transient absorptions in the same spectral ranges, but the signal intensities were 2−3 times stronger than those from **1**. The trace recorded at 550 nm (Figure 3) decays with kinetics similar to that observed from NLFP of **1** under similar conditions and
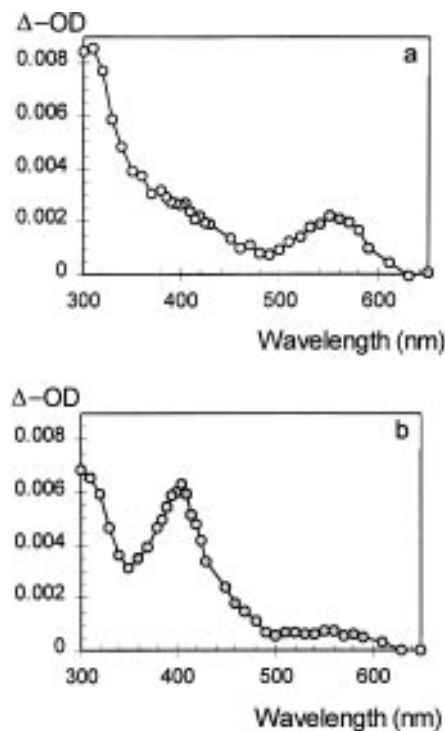

Figure 2. Transient UV absorption spectra, from nanosecond laser flash photolysis of **1** under the same conditions as in Figure 1. Spectrum a was recorded 0−2 μs after the laser pulse, while spectrum b was recorded over the last 10% of the monitored time window.
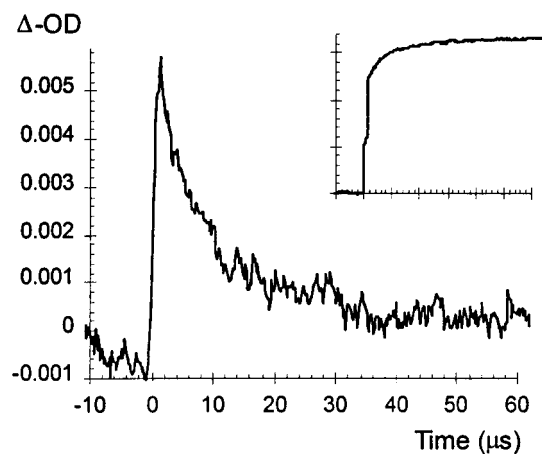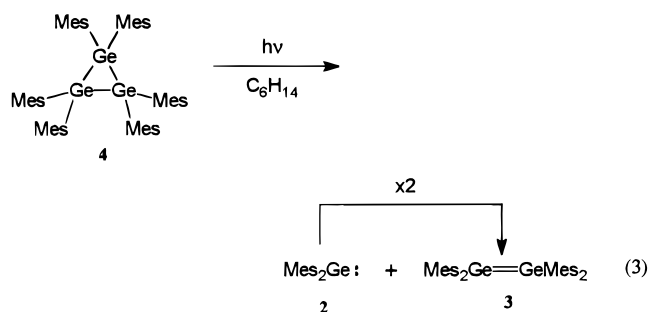

Figure 3. Transient decay trace, from nanosecond laser flash photolysis of a deoxygenated, ca. 4×10^{-5} M solution of **4** in hexane at 23 °C, recorded at a monitoring wavelength of 550 nm. Insert: growth trace monitored at 405 nm.

is also assigned to dimesitylgermylene. The trace recorded at 405 nm exhibits an "instantaneous" jump (evident in traces recorded using a faster time scale) followed by a slow second-order growth to a stable residual absorption level. Parts a and b of Figure 4 show the transient absorption spectra recorded "immediately" (i.e. 0−2 μs) and at 50−60 μs after laser excitation; the difference spectrum is shown in Figure 4c. Figure 4a is similar to the spectrum reported by Masamune and co-workers from low-temperature photolysis of similar hexaarylcyclotrigermanes.[17] The temporal behavior of the 405 nm absorption is consistent with digermene **3** being formed both "instantaneously" (i.e., in the initial photolytic event) and over longer time

scales due to the dimerization of the germylene **2** (eq 3). NLFP of cyclotrigermane **4** with monitoring in the

$$
\begin{array}{c}
\text{Mes}\quad\text{Mes}\\
\text{Ge}\\
\text{Mes}-\text{Ge}-\text{Ge}-\text{Mes}\\
\text{Mes}\quad\text{Mes}\\
\mathbf{4}
\end{array}
\xrightarrow[\text{C}_6\text{H}_{14}]{h\nu}
$$

$$
\overset{\times 2}{\underset{\mathbf{2}}{\text{Mes}_2\text{Ge}:}} + \underset{\mathbf{3}}{\text{Mes}_2\text{Ge}=\text{GeMes}_2} \quad (3)
$$

270−310 nm range showed evidence for irreversible bleaching of the precursor, with no recovery of the signal that could be attributed to recombination of the primary products: Mes_2Ge and the digermene **3**.

The spectrum shown in Figure 4c was determined by subtracting 76% of the intensity of Figure 4b from that of Figure 4a. It corresponds well with that shown in Figure 2a (obtained from the photolysis of the bis(silyl)-germane **1**), except for the sharp cutoff at ∼325 nm, which corresponds to the onset of the absorption spectrum of the cyclotrigermane **4** and is due to the bleaching phenomenon discussed above. The correction factor used is somewhat higher than the value (66.7%) that would be predicted according to eq 3 for the formation of digermene **3**. The additional correction is necessary because the spectrum of Figure 4a represents the average over an initial time *window* after excitation, during which **3** is formed via the dimerization of **2**.

Saturation of the solution of cyclotrigermane **4** with oxygen results in marked shortening of the lifetimes of the transients observed at both 550 and 405 nm; in both cases, the absorptions decay with clean pseudo-first-order kinetics and decay rate constants of $(1.1 \pm 0.1) \times 10^5$ and $(3.4 \pm 0.5) \times 10^3$ s^{-1}, respectively. Using a value of 0.015 M for the concentration of oxygen in oxygen-saturated hexane,[18] we obtain estimated values of $(7.3 \pm 0.8) \times 10^6$ and $(2.3 \pm 0.4) \times 10^5$ M^{-1} s^{-1} for the rate constants for reaction of oxygen with germylene **2** and digermene **3**, respectively.

Addition of triethylsilane or 1-bromohexane to the hexane solution of cyclotrigermane **4** resulted in shortening of the lifetime of the 550 nm transient and a change to pseudo-first-order decay kinetics but had no effect on its initial yield. The decay rate constant of the transient varied linearly with the concentration of added reagent ("Q"); least-squares analyses of plots of k_{decay} *vs* quencher concentration according to eq 4 (where $k_d{}^0$,

$$k_{decay} = k_d{}^0 + k_q[Q] \quad (4)$$

the pseudo-first-order decay rate constant in the absence of quencher, is indeterminable in this case) afford the corresponding bimolecular rate constants (k_q) for reaction of the transient with the two quenchers. The values obtained are $k_q = (1.1 \pm 0.1) \times 10^5$ M^{-1} s^{-1} for triethylsilane and $k_q = (5.4 \pm 0.5) \times 10^5$ M^{-1} s^{-1} for 1-bromohexane. Figure 5 shows a representative quenching plot for triethylsilane. Addition of these reagents

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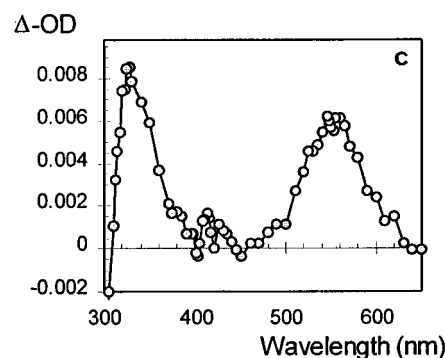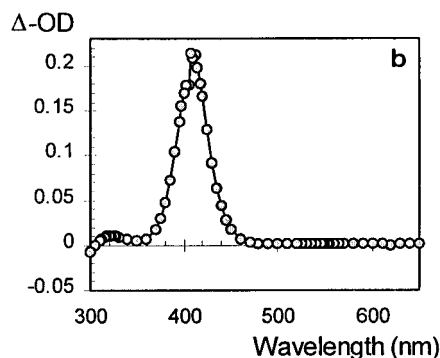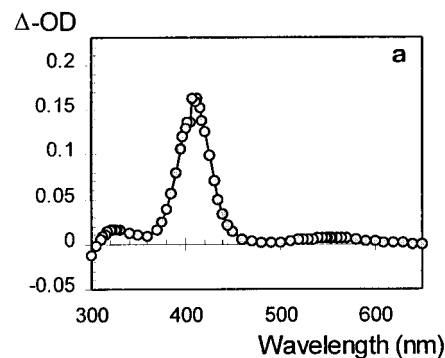

Figure 4. Transient UV absorption spectra, from nanosecond laser flash photolysis of **4** under the same conditions as in Figure 3. Spectrum a was recorded 0−2 μs after the laser pulse, while spectrum b was recorded over the last 10% of the monitored time window. The scaled difference spectrum ((a) − 0.76(b)) is shown in (c).
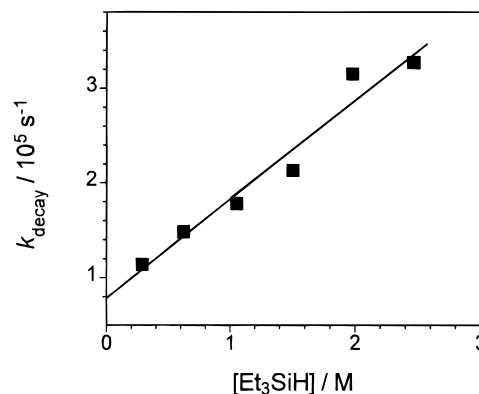

Figure 5. Plot of the pseudo-first-order rate constant for decay (k_{decay}) of the 550 nm transient from NLFP of **4** in triethylsilane−hexane at 23 °C, versus [Et$_3$SiH].

also has an effect on the 405 nm absorption due to the digermene **3**, in that the instantaneous jump in absorption that occurs with the laser pulse is not followed by

Table 1. Rate Constants for the Quenching of Germylenes

λ_{max} (nm)	assignt	rate constant (M^{-1} s^{-1})				ref
		O_2	R_3SiH	ROH	RBr	
550	Mes_2Ge	$(7.3 \pm 0.8) \times 10^6$	R = Et, $(1.1 \pm 0.1) \times 10^5$	R = Et[a]	R = hexyl, $(5.4 \pm 0.5) \times 10^5$	this work
445	Ph_2Ge	$(1.02 \pm 0.08) \times 10^8$	$R_3 = Me_2Et$, $(1.01 \pm 0.03) \times 10^4$	R = Me[a]	R = isobutyl, $(6.36 \pm 0.21) \times 10^5$	12
450	Ph_2Ge	b	R = Et, 6.6×10^5	R = Et[a]	b	14f,g
470	Ph_2Ge	1.8×10^8	b	R = Et[a]	b	14d,h
450	PhMeGe	2.3×10^8	b	R = Et[a]	b	14d,h
440	PhMeGe	b	R = Et, 4.1×10^6	R = Et[a]	b	14f,g
420	Me_2Ge	b	R = Et, 4.2×10^6	R = Et[a]	b	14f,g
450	Me_2Ge	9.7×10^8	b	b	b	14c
490	Me_2Ge	1.6×10^9	b	b	b	14b
425	Me_2Ge	2×10^9	R = Et, $<10^4$	$(1.86 \pm 0.12) \times 10^4$	b	13
430	Me_2Ge	2.1×10^9	b	R = Et[a]	b	14e
430	Me_2Ge	1.7×10^9	b	R = Et[a]	b	14e
580	Mes_2Si	$(3.2 \pm 0.4) \times 10^7$	R = Et, $(7.9 \pm 0.4) \times 10^7$	b	b	16

[a] Not quenched. [b] Not measured.

a growth to a higher level. There is no effect on the lifetime of the digermene **3**, however. In similar experiments with the bis(silyl)germane **1**, addition of oxygen, triethylsilane, or 1-bromohexane caused similar reductions in the lifetime of the 550 nm transient (**2**) and resulted in the disappearance of the absorption at 405 nm. Addition of up to 1.5 M ethanol to hexane solutions of **1** and **4** had no discernible effect on the yields or temporal characteristics of either species.

Discussion

There have been relatively few absolute rate constants reported in the literature for germylene trapping reactions in solution. However, data common to dimethyl-, methylphenyl-, and diphenylgermylene do exist for oxygen, triethylsilane, ethanol, and (to a lesser extent) primary bromoalkanes, and thus, these were selected as representative trapping agents in the present study of dimesitylgermylene (**2**). Table 1 summarizes our absolute rate constants for reaction of the 550 nm transient with these four reagents and, for comparison purposes, literature data for the other three germylenes and for dimesitylsilylene. As can be seen, there is good qualitative agreement with the reported data for diphenylgermylene, consistent with the assignment of the 550 nm transient as Mes_2Ge.

The reactivity of diorganogermylenes toward oxygen is well-recognized, yet there have been relatively few studies on the nature of the products. The few that exist are consistent with the formation of the corresponding germanone, presumably via the intermediacy of the germanone oxide. For example, Satgé and co-workers have found that PhClGe reacts with oxygen to give a germoxane polymer, $(-PhClGeO-)_n$,[19] and a cyclodigermoxane has been isolated from reaction of a sterically encumbered diaminogermylene with oxygen.[20] Products have evidently not been reported for any of the germylenes included in Table 1. As might be expected on the basis of steric considerations, the absolute rate constant determined herein for reaction of Mes_2Ge with O_2 in hexane solution is roughly 1 order of magnitude lower than the corresponding values for

diphenylgermylene in cyclohexane[12] and THF,[14d,h] 30 times less than that for PhMeGe in THF[14d,h] and 2 orders of magnitude lower than those for Me_2Ge in cyclohexane.[13,14b,c,e] It is interesting to note that Mes_2-Ge and Mes_2Si react with oxygen with very similar rates.

Mes_2Ge, generated by the thermolysis or photolysis of Ge_3Mes_6[4] or $SiGe_2Mes_6$,[2] can be trapped in high yield by insertion into the Si–H bond of triethylsilane to give $Mes_2GeHSiEt_3$.[21] There are discrepancies in the absolute rate constants for reaction of Ph_2Ge with trialkylsilanes reported by Mochida[14f,g] and Gaspar[12] and their co-workers, although the latter pointed out the possibility of problems with their data.[13] Thus, the value of $\sim 7 \times 10^5$ M^{-1} s^{-1} for the reaction between Ph_2Ge and Et_3SiH in cyclohexane of the Mochida group is likely to be the more reasonable value, as it is 6 times faster than the present value for Mes_2Ge with the same silane in hexane. The difference in reactivity between Ph_2Ge and Mes_2Ge toward triethylsilane is similar to the difference in reactivity of the two germylenes toward oxygen. Unlike oxygen, however, Mes_2-Ge is about 2 orders of magnitude less reactive than Mes_2Si[16] toward Si–H insertion, which more properly reflects the difference in the stabilities of germylenes and silylenes.[22]

There is general agreement that alcohols react so sluggishly with diaryl- and dialkylgermylenes that it is difficult to measure a rate constant.[12,14] We obtain similar results for Mes_2Ge, where addition of up to 1.5 M ethanol has no discernible effect on the decay kinetics of the germylene in deoxygenated hexane solution. Since we would be able to detect a change of as small as 10% in the transient decay rate of Mes_2Ge in our experiments, we can estimate an upper limit of $<10^3$ M^{-1} s^{-1} for the rate constant for the reaction of Mes_2-Ge with ethanol in hexane. While a rate constant for reaction of Mes_2Si with alcohols has not been reported, data for other systems suggest that germylenes are orders of magnitude less reactive than the correspond-

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Table 2. Rate Constants for the Quenching of Digermenes

λ_{max} of transient abs (nm)	assignt	rate constant for quenching by O_2 ($M^{-1} s^{-1}$)	ref
405	$Mes_2Ge{=}GeMes_2$	$(2.3 \pm 0.4) \times 10^5$	this work
370	$Me_2Ge{=}GeMe_2$	2.8×10^8	14c
370	$Me_2Ge{=}GeMe_2$	1.8×10^8	14b

ing silylenes toward alcohols in solution.[14d–h,23] In spite of this sluggish reactivity, the formation of alkoxygermanes (RO)GeMes$_2$H in the thermolysis or photolysis of Mes$_2$Ge precursors in the presence of methanol[1,24] or ethanol[9] has been reported by several groups.

Dimethylgermylene is known to insert into the carbon–halogen bond of some alkyl halides such as CCl$_4$ and PhCH$_2$X (X = Br, I) via a halogen abstraction/radical recombination process and into the C-Cl bond of allyl chloride via a one-step mechanism.[25] Interestingly, no reaction was observed between saturated alkyl bromides and Me$_2$Ge. Mes$_2$Ge has been reported to insert into the C–Cl bond of allyl chloride,[9] and Gaspar and co-workers have reported a value of $\sim 6 \times 10^5$ M^{-1} s^{-1} for the reaction of Ph$_2$Ge with isobutyl bromide.[12] This is very similar to the value reported here for reaction of Mes$_2$Ge with 1-bromohexane ($k \approx 5 \times 10^5$ M^{-1} s^{-1}).

In spite of the well-known reactivity of digermenes toward oxygen,[26] there have been only two reports of absolute rate constants for such reactions and both are for tetramethyldigermene[14b,c] (see Table 2). Mes$_2$-Ge=GeMes$_2$ is roughly 3 orders of magnitude less reactive toward oxygen than the tetramethyl derivative, which can be attributed to the stabilizing influence (probably both steric and electronic) of the mesityl substituents.

The above comparison of the reactivities of the divalent silicon and germanium species reveals several fascinating trends, which are the subject of further collaborative study in our laboratories.

Experimental Section

Dimesitylbis(trimethylsilyl)germane[27] and hexamesitylcyclotrigermane[28] were prepared according to literature procedures and were purified by repeated crystallizations from ethanol/hexanes or hexanes, respectively. Nanosecond laser flash photolysis experiments employed the pulses (248 nm, 80–120 mJ, ca. 16 ns) from a Lumonics 510 excimer laser filled with F$_2$/Kr/He mixtures and a microcomputer-controlled detection system.[29,30] The system employs a pulsed 150 W high-pressure Xe lamp as the spectral source for experiments employing time scales of <500 μs full scale; experiments employing the 0.5–5 ms time range were carried out without the pulser. Solutions were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was ca. 0.7 (10^{-4}–10^{-3} M) and were flowed continuously through a 3 $\times$ 7 mm Suprasil flow cell connected to a calibrated 100 mL reservoir. The flow cell was mounted in a thermostated sample holder whose temperature was controlled to within 0.1 °C by a refrigerated circulating bath; temperatures were measured by means of a copper–constantan thermocouple (Omega, Inc.) inserted directly into the flow cell through its exhaust port. The solutions were deoxygenated continuously in the reservoir with a stream of dry nitrogen. Quenchers 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 (6–10 points), which spanned at least 1 order of magnitude in the transient decay rate. Errors are quoted as twice the standard deviation obtained from the least-squares analysis in each case.

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