

Photochemistry of Group 14 1,1,1-Trimethyl-2,2,2-triphenyldimetallanes (Ph₃MM'Me₃; M, M' = Si, Ge). Direct Detection and Characterization of Silene and Germene Reactive Intermediates

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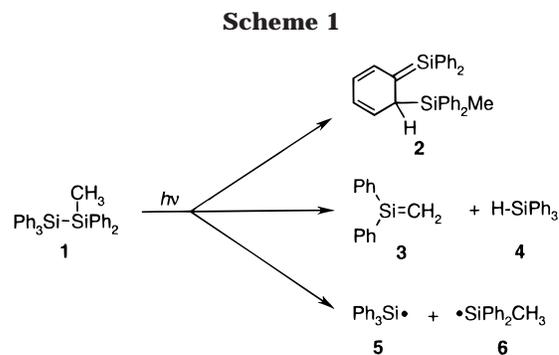
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Received February 24, 2000

The photochemistry of trimethylsilyltriphenylgermane (Ph₃GeSiMe₃), triphenylsilyltrimethylgermane (Ph₃SiGeMe₃), and 1,1,1-trimethyl-2,2,2-triphenyldigermene (Ph₃GeGeMe₃) has been studied in hydrocarbon solution by steady state and laser flash photolysis methods and is compared to previously reported data for the homologous disilane Ph₃SiSiMe₃. A variety of products are formed upon photolysis of the three compounds in the presence of 2,3-dimethyl-1,3-butadiene or chloroform, but in each case the major ones are derived from M–M' bond homolysis and dimethyl- or diphenylgermylene extrusion. The trapping products of the 1,3,5-(1-metalla)hexatriene derivatives formed by [1,3]-MMe₃ migration into the ortho-position of one of the phenyl rings are formed as well, in yields of 9–30%. While these experiments indicate that germynes are formed in at least twice the yield of the 1,3,5-(1-metalla)hexatrienes, only the latter and triphenylsilyl or triphenylgermyl radicals can be detected by laser flash photolysis techniques. The metallaenes have been identified on the basis of their time-resolved UV absorption spectra and absolute rate constants for reaction with 2,3-dimethylbutadiene, methanol, acetone, acetic acid, oxygen, and carbon tetrachloride and can be distinguished from germynes by their lack of reactivity toward triethylsilane and chloroform. Radical formation is shown to result from reaction of the triplet states of these compounds, and a triplet lifetime is estimated for Ph₃GeSiMe₃ and compared to that of the disilane homologue. The results of time-resolved experiments on other, related compounds are discussed in light of these results.

Introduction

The photochemistry of aryldisilanes has been extensively investigated over the past 25 years.^{1–5} In general, photolysis of these compounds leads to the formation of three distinct types of reactive intermediates, in relative yields that vary markedly depending on the degree of aryl substitution in the disilane and on the solvent. This complexity is most aptly demonstrated by the photochemistry of methylpentaphenyldisilane (**1**), which yields silenes **2** and **3** by [1,3]-SiPh₂Me migration and dehydrosilylation (elimination of H–SiPh₃ (**4**)), respectively, and the silyl free radicals **5** and **6** by Si–Si bond homolysis (Scheme 1).^{6–8} The formation of



the (1-sila)hexatriene **2** by concerted^{9,10} [1,3]-silyl migration is relatively minor in **1**, but is quite frequently the major photoreaction of aryldisilanes in solution.^{7,11–19}

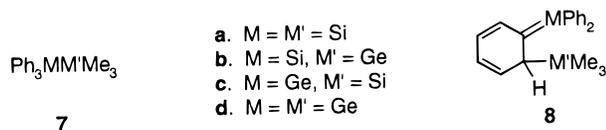
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The opposite is true of the dehydrosilylation reaction to produce silene **3**. Both these reaction pathways are singlet-derived; silyl free radical formation results from the triplet state of the disilane and hence can be made to predominate either by enhancing intersystem crossing through adjustment of the solvent polarity¹⁷ or by slowing down the singlet-derived reaction pathways by attaching sterically bulky substituents.²⁰

Disilanes are the simplest congeners of higher oligo- and polysilanes, whose photochemical and photophysical behavior has also been of considerable interest.^{21–23} The photochemistry of trisilanes and higher oligosilanes is usually characterized by predominant extrusion of silylene reactive intermediates,²⁴ a process of relatively minor importance in aryldisilanes except in the presence of special structural constraints.²⁵

Laser flash photolysis studies of aryldisilanes have provided a wealth of mechanistic information on the reactions of transient silenes with various "silenophiles" such as alcohols, ketones and aldehydes, carboxylic acids, dienes, and oxygen, as well as important insight into various aspects of disilane photophysics and the effects of substituents on disilane photochemistry.^{7,8,17,19,20,26,27} 1,1,1-Trimethyl-2,2,2-triphenyldisilane (**7a**) has proven to be particularly useful in this regard.^{17,19,26,27} In hydrocarbon solvents, photolysis of **7a** yields cleanly and in high yield the (transient) 1,1-diphenyl-(1-sila)hexatriene derivative **8a**, which can easily be detected and studied by such methods. In contrast, photolysis in more polar solvents leads to high yields of the corresponding silyl free radicals, with **8a** being formed in low (but still detectable) amounts. The remarkable sensitivity of the photochemistry of this compound to solvent polarity provided the impetus for the discovery that silyl free radicals are formed via the triplet states of aryldisilanes and are not precursors to silene products (at least on the $>10^{-8}$ s time scale).¹⁷ The reactivity of **8a** also proved to be unusual, owing to unique steric constraints which serve to direct the chemistry of the Si=C bond along pathways that are often only minor in other aryldisilane-derived silenes. This allowed, for example, the isolation of stable 1,2-siloxetanes from reaction with acetone and other ketones and provided much detail on the mechanism of this well-known (but seldom fruitful) reaction of transient silenes.^{17,26,27}



In this paper, we report the results of a study of the photochemistry of the trimethyltriphenylgermasilane

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derivatives **7b,c** and of 1,1,1-trimethyl-2,2,2-triphenyldigermene (**7d**) by steady state and laser flash photolysis techniques. Our intent was to examine, in a systematic way, the changes induced in the photochemistry of **7a** as a result of replacement of first one and then both of the silicon atoms with germanium. We anticipated (based on literature precedent; vide infra) that photolysis of these compounds might afford the corresponding (1-metalla)hexatriene reactive intermediates **8b–d** in high enough yields that they might be detected by flash photolysis methods, thus affording the opportunity to broaden the scope of our studies of the differences in the reactivity of silicon- and germanium-carbon double bonds.^{28,29}

Previously reported work on **7d**³⁰ and a related series of compounds (**9b–d**) by Mochida and Gaspar and their co-workers^{31,32} suggests that reactive intermediates of this type are formed in significant yields in the photolysis of arylgermasilanes, but in minor amounts relative to silyl and/or germyl radicals and dimethylgermylene. Germylene formation is even more dominant in the photochemistry of Fe^{II}-germasilane and -silagermane complexes, where the efficiency of the reaction appears to not depend greatly on which of the two group 14 atoms is attached to the metal center. For example, irradiation of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiMe}_2\text{GeMe}_3$ and its isomer $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{GeMe}_2\text{SiMe}_3$ each results mainly in elimination of Me_2Ge with concomitant formation of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiMe}_3$.³³

Laser flash photolysis experiments on **9b–d** verified that free radical formation dominates the photochemistry of these compounds and allowed the detection of an additional transient product absorbing in the 400–460 nm region of the spectrum, which was assigned to dimethylgermylene.^{31,32} On the basis of our and others experience with the disilane analogue **9a**^{7,16,19,26} and a recently acquired knowledge of the quantitative aspects of transient germene reactivity,^{28,29} it seemed possible to us that these transients might better be assigned to the (1-germa)hexatriene species **10c,d**. This suspicion provided further justification for the present study of **7b–d**, since the corresponding transient 1,1-diphenyl-(1-metalla)hexatrienes, if obtained, would be expected to exhibit absorption maxima at significantly longer wavelengths than those that have been reported by various workers (under a variety of conditions) for either Me_2Ge .^{32,34–37} or Ph_2Ge .^{30,35,36,38}

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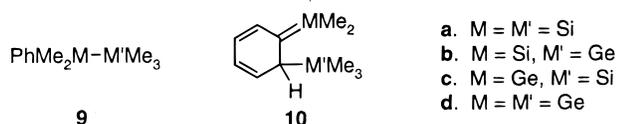
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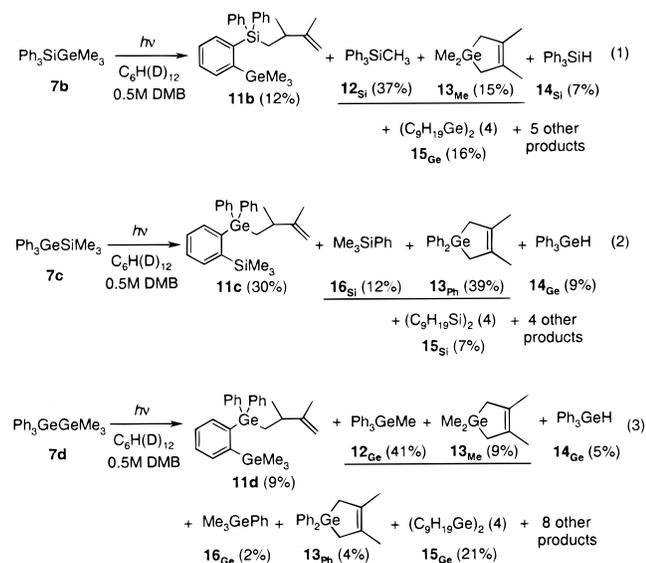
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- a.** $\text{M} = \text{M}' = \text{Si}$
b. $\text{M} = \text{Si}, \text{M}' = \text{Ge}$
c. $\text{M} = \text{Ge}, \text{M}' = \text{Si}$
d. $\text{M} = \text{M}' = \text{Ge}$

Results and Discussion

Steady State Photolysis and Trapping of Reactive Intermediates. Photolysis of deoxygenated cyclohexane solutions of **7a** (0.05 M) in the presence of 2,3-dimethyl-1,3-butadiene (DMB) affords the silatriene–DMB adduct **11a** in ~70% yield, along with minor amounts of an unidentified isomeric adduct.¹⁹ In contrast, photolysis of **7b–d** under similar conditions in each case afforded complex mixtures of more than a dozen products; those that we have been able to identify, either by GC co-injection with authentic samples, after isolation by semipreparative GC, or by GC/MS on the basis of comparisons to literature data, are shown in eqs 1–3. The product yields listed were determined by



GC/MS after 30–50% conversion of starting material, as simple percentages of the total detectable products, and are uncorrected for differences in detector response factors.³⁹ This method underestimates the yields of the relatively low molecular weight products (**13_{Me}** and **16**) because they elute much earlier than the starting material and other products. This was verified by ¹H NMR spectroscopy on crude photolysis mixtures in C₆D₁₂ solution, which showed the yields of **12** to be similar to those of **13** in the photolyses of **7b,d**; the same was found to be true of the relative yields of **13** and **16** in the photolyses of **7c,d**. The three photolysates also contained several other minor products, each of which were formed in yields of less than ~3%. The material balances (starting material + identified products) were

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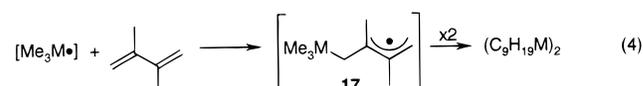
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determined to be on the order of 65–75% after ca. 50% conversion of starting material in all three cases.

Compounds **11b** and **11c**, which were isolated, exhibited spectroscopic data similar to those reported previously for **11a**¹⁹ and the DMB adducts of **10b,c**.^{31,32} A pure sample of **11d** could not be isolated in sufficient quantities for rigorous characterization and so was identified on the basis of comparisons of its GC retention time to those of **11a–c** and its mass spectrum (obtained by GC/MS) to that of **11c**. The mass spectra of both **11c** and **11d** exhibit parent ions at M-83 due to loss of C₆H₁₁ from the molecular ion, a fragmentation pathway that is relatively minor in compounds **11a,b**. The product mixtures also contained four isomeric compounds with similar but slightly lower GC retention times than the precursors (**7**); these are collectively identified in eqs 1–3 as **15_{Ge}** (from **7b,d**) and **15_{Si}** (from **7c**). They were tentatively identified on the basis of their mass spectra as dimers of the carbon-centered free radicals (**17**) derived from addition of Me₃M• to the diene, as shown in eq 4. The mass spectra of the four (C₉H₁₉Si)₂ isomers



(**15_{Si}**) are identical and exhibit a weak molecular ion (M⁺ = 310), prominent (M/2)⁺ ions, and a (M⁺ = 73) parent ion due to Me₃Si. The spectra of the germanium analogues (**15_{Ge}**) are also identical to one another and contain the M⁺ = 119 (Me₃Ge) parent ion, but show only the (M/2)⁺ ion in the higher mass range. The relative yields of the four isomeric products were the same from **7b** and **7d**. The corresponding products from trapping of Ph₃M• radicals were not detected in the photolysates, not unexpectedly considering their very high molecular weights.

The mechanism for formation of Ph₃M–H (**14_{Si}** and **14_{Ge}**) is not clear. The mass spectra of these compounds formed in the photolyses of **7b–d** in C₆H₁₂ and C₆D₁₂ indicated that no deuterium was incorporated in either of these products in the deuterated solvent, indicating that they are not formed from reaction of Ph₃M• radicals with the solvent. Furthermore, no evidence could be obtained for the presence of products that might be consistent with disproportionation of Ph₃M• and **17** in any of the three cases. Since these products would have the same molecular formula as those derived from trapping of Me₂M=CH₂ by the diene (C₉H₁₈M), we can similarly rule out the possibility that **14** is formed by either Ph₃M•/Me₃M• disproportionation or concerted dehydrometalation. At an early point in the study, photolyses of **7b–d** were carried out in hexane containing *n*-decanol (0.1 M), to probe for the formation of Me₂M=CH₂ by trapping with the alcohol. The expected alkoxymetallanes (**18**) are indeed formed under these conditions, but are accompanied by increased yields of **14** in all three cases. Thus, the most likely mechanism for formation of **18** in these experiments is direct reaction of the alcohol with the excited singlet states of **7b–d**, a reaction that is particularly well established to occur with aryldisilanes.^{26,40} We have not explored the point further.

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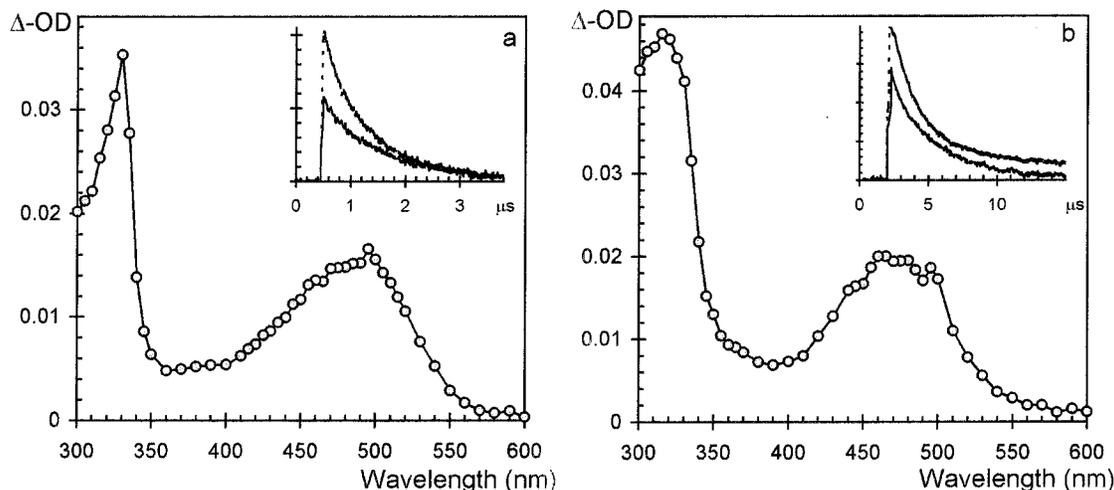


Figure 1. Time-resolved UV absorption spectra recorded with deoxygenated 5.0×10^{-4} M solutions of $\text{Ph}_3\text{SiGeMe}_3$ (**7b**, a) and $\text{Ph}_3\text{GeSiMe}_3$ (**7c**, b) in hexane at 23 °C, 0.2–1.0 μs after 248 nm pulsed laser excitation. The insets show decay traces recorded at monitoring wavelengths of 330 (---) and 490 nm (—).

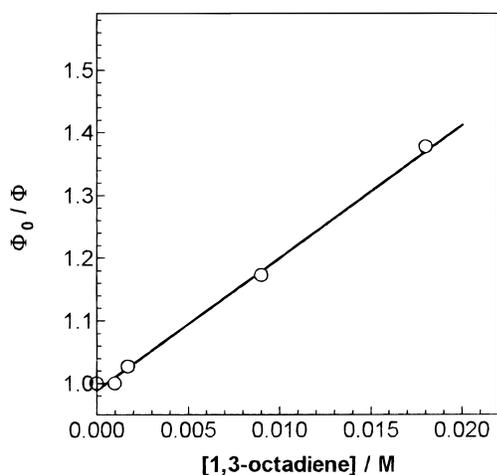


Figure 2. Stern–Volmer plot of the ratios of the ΔODs at 330 and 490 nm (Φ_0/Φ ; see eq 6), from photolysis of **7b** in the presence of 1,3-octadiene (0–0.02 M).

Addition of methanol (MeOH), DMB, acetone, acetic acid, carbon tetrachloride, or oxygen to the solutions of $\text{Ph}_3\text{SiGeMe}_3$ (**7b**) resulted in an increase in the pseudo-first-order rate constant for decay of the long-wavelength transient absorption. Plots of k_{decay} versus concentration of added reagent were curved for methanol (Figure 3a), but fit acceptably to the second-order polynomial expression shown in eq 7, where k_d^0 is the

$$k_{\text{decay}} = k_d^0 + k_{\text{MeOH}}[\text{MeOH}] + k_{2\text{MeOH}}[\text{MeOH}]^2 \quad (7)$$

decay rate constant in the absence of methanol, and k_{MeOH} and $k_{2\text{MeOH}}$ are the overall second- and third-order rate constants for reaction of the transient with the alcohol. Similar plots for the other reagents were linear in concentration and were thus analyzed according to eq 8. Representative plots of k_{decay} vs concentration for

$$k_{\text{decay}} = k_d^0 + k_q[\text{Q}] \quad (8)$$

the quenching of the long wavelength transient from **7b** by MeOH, acetic acid, DMB, and acetone are shown in Figure 3. Of the six reagents examined, only oxygen,

DMB, and carbon tetrachloride affected the lifetime of the triphenylsilyl radical absorption at 330 nm as well as that of the longer wavelength transient. In contrast, addition of chloroform to the solution had no effect on the lifetime of the long wavelength transient absorption within the concentration range examined ($[\text{CHCl}_3] < 0.02$ M), but quenched that of the radical efficiently (vide supra).

The lifetime of the 480 nm transient absorption from photolysis of $\text{Ph}_3\text{GeSiMe}_3$ (**7c**) was also quenched upon addition of DMB, HOAc, acetone, carbon tetrachloride, or oxygen, but with the exception of the halocarbon, quenching was much less efficient than with the analogous transient from **7b**. The decay rate constants varied in direct proportion to concentration of added reagent in each case, as is illustrated by the quenching plots shown in Figure 4 for reaction of the transient with acetic acid, DMB, and acetone. Again, addition of up to ~ 0.06 M chloroform had no effect on the lifetime of the long wavelength absorption, but quenched the radical absorption at shorter wavelengths. Addition of up to 1.7 M MeOH had no discernible effect on the lifetimes at either monitoring wavelength.

The transient absorption spectrum recorded by flash photolysis of a deoxygenated hexane solution of $\text{Ph}_3\text{GeGeMe}_3$ (**7d**) showed similarities to those from the other two compounds (Figure 5a), but the long wavelength absorption band was significantly less intense than the short wavelength absorption at 330 nm. Still, transient decays recorded at the two wavelengths showed marked differences in lifetime, indicating that two different transient species are being observed. As with **7c**, addition of 0.065 M chloroform to the solution shortens the lifetime of the 330 nm transient to < 25 ns (consistent with its assignment to triphenylgermyl radicals) but has little effect on that of the 480 nm transient ($\tau \approx 2.5 \mu\text{s}$). This allows isolation of the spectrum due to the long-wavelength-absorbing species, as is shown in Figure 5b. Addition of DMB, carbon tetrachloride, or oxygen to the chloroform/hexane solutions of **7d** resulted in shortening of the lifetime of this transient, and the transient decay rate varied linearly with concentration. Quenching by HOAc, acetone, and MeOH was not investigated in this case.

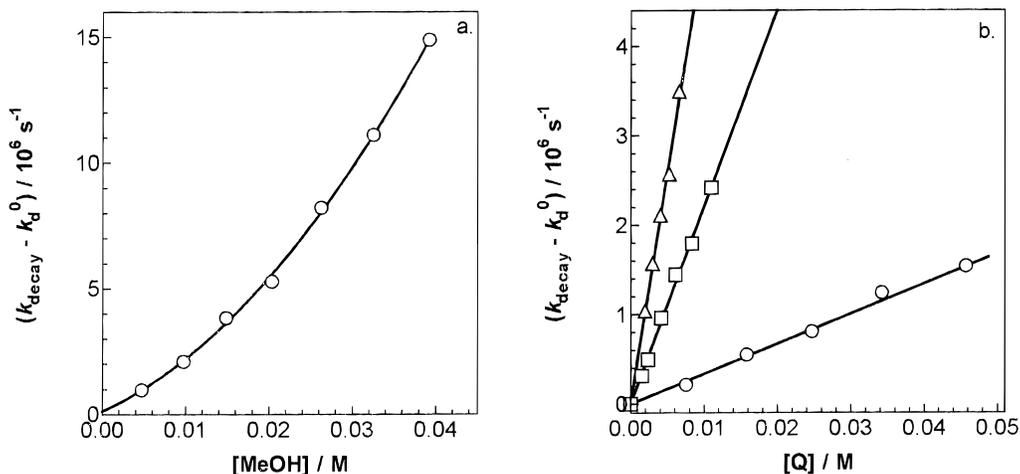


Figure 3. Stern–Volmer plots for quenching of silene **8b** by (a) methanol and (b) acetic acid (\square), 2,3-dimethyl-1,3-butadiene (\circ), and acetone (\triangle) in deoxygenated hexane solution at 23 °C. The solid lines represent the best fits of the data to eqs 7 (a) and 8 (b).

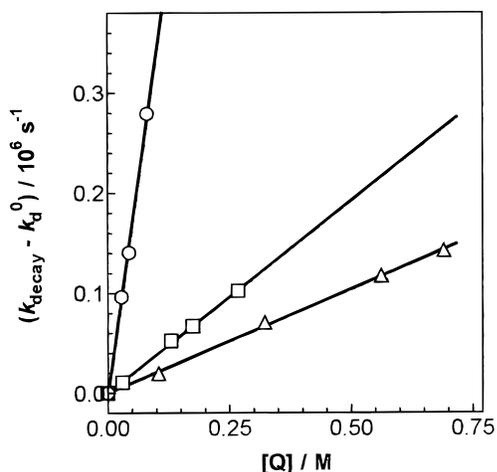


Figure 4. Stern–Volmer plots for quenching of germene **8c** by acetic acid (\square), 2,3-dimethyl-1,3-butadiene (\circ), and acetone (\triangle) in deoxygenated hexane solution at 23 °C. The solid lines represent the best fits of the data to eq 8.

Table 1 summarizes the absolute rate constants for quenching of the 480–490 nm transient absorptions from flash photolysis of **7b–d** by the six quenchers studied, along with the analogous data for quenching of the transient 1-silahexatriene (**8a**) derived from **7a** in the same solvent.^{19,26} Addition of up to 4 M triethylsilane (HSiEt_3) to the solutions of **7b,c** had no effect on the lifetimes of either the radicals or the long-wavelength-absorbing transients; upper limits for the rate constants for quenching of the 480 nm transients from these two compounds, calculated from the lifetimes in the absence and presence of 4 M silane, are included in Table 1 along with analogous data for **8a**.

The 490 nm transient obtained from **7b** exhibits an absorption spectrum nearly identical to that of **8a** and strikingly similar rate constants for reaction with all six of the quenchers examined, suggesting it should be assigned to the 7-trimethylgermyl-substituted 1-silahexatriene derivative **8b**. The similarities in the UV spectra and reactivity of **8a** and **8b** are quite reasonable, given that the only structural difference between the two molecules is the Me_3M substituent at the 7-position of the 1-metallahexatrienyl moiety. The alternative

assignment of this transient to Me_2Ge , which our product studies show is formed in roughly twice the yield of **8b** (eq 1), can be ruled out on the basis of several arguments. First, dimethylgermylene has been reported to exhibit an absorption maximum in the 420–450 nm range in hydrocarbon solvents at room temperature,^{32,36,37,44} significantly lower than the absorption maximum of the transient obtained from germsilane **7b**. Second, the transient shows the same high reactivity toward methanol (and the other five reagents) as **8a**; dimethylgermylene is known to be relatively unreactive toward alcohols ($k_{\text{ROH}} \ll 10^4 \text{ M}^{-1} \text{ s}^{-1}$).^{37,44} Third, the transient shows no detectable reactivity toward triethylsilane and chloroform, reagents which are known or can be expected to react rapidly with Me_2Ge .^{37,45} Finally, the extinction coefficient of the long wavelength (π, π^*) absorption of the 1-silahexatriene (**8b**) can be expected to be at least an order of magnitude larger than that of the (n,p) absorption of dimethylgermylene; this leads to the expectation that the absorption due to **8b** should be at least 5 times greater than for the germylene, given they are formed in relative yields of 1:2.⁴⁶

Similarly, we assign the 480 nm transient products observed by flash photolysis of **7c,d** to the 1-germahexatrienes **8c,d**. These two compounds can be expected to exhibit absorption maxima and extinction coefficients similar to the silicon analogues **8a,b**, since 1,1-diphenylsilene (**23a**) and 1,1-diphenylgermene (**23b**) exhibit nearly identical UV absorption spectra in hydrocarbon solvents ($\lambda_{\text{max}} = 325 \text{ nm}$,^{28,29} $\epsilon_{\text{max}} = 7500\text{--}11\,000 \text{ M}^{-1} \text{ cm}^{-1}$).⁴⁷ The transient assigned as **8c** also exhibits the expected decrease in reactivity compared to **8a,b** toward the nucleophilic quenchers MeOH, HOAc, and acetone, judging from a comparison of the absolute reactivities of **23a** and **23b** toward these same reagents.^{28,29} While

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(46) The extinction coefficient at the absorption maximum for dimesitylgermylene is approximately 15 times less than that of tetramesityldigermene, on the basis of experiments in which the two species are generated together in a 1:1 ratio. See: Tolft, N. P.; Leigh, W. J.; Kolleger, G. M.; Stibbs, W. G.; Baines, K. M. *Organometallics* **1996**, *15*, 3732. The extinction coefficient of tetramesityldigermene at its absorption maximum is ca. $20\,000 \text{ M}^{-1} \text{ cm}^{-1}$ (Baines, K. M. private communication). Thus, this allows an estimate of $800 \pm 400 \text{ M}^{-1} \text{ cm}^{-1}$ for the extinction coefficient of dimesitylgermylene.

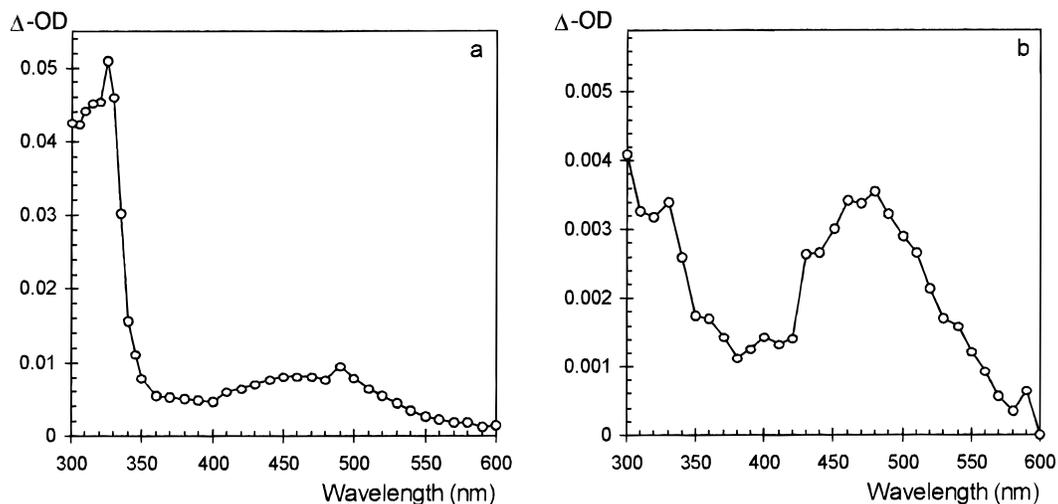
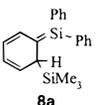
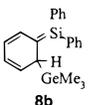
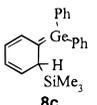
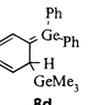


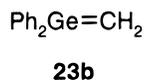
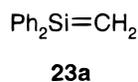
Figure 5. Time-resolved UV absorption spectra recorded with deoxygenated 5.0×10^{-4} M solutions of $\text{Ph}_3\text{GeGeMe}_3$ (**7d**) at 23 °C in (a) hexane and (b) hexane containing 0.07 M chloroform. The spectra were recorded 0.2–1.0 μs after 248 nm pulsed laser excitation.

Table 1. Absolute Rate Constants (in units of $10^8 \text{ M}^{-1} \text{ s}^{-1}$) for Quenching of Transient 1-Metallahexatrienes (8a–d**) by 2,3-Dimethyl-1,3-butadiene (DMB), Acetone, Acetic Acid, Methanol, Oxygen, Carbon Tetrachloride, and Triethylsilane in Hexane Solution at 23 °C^a**

| Quencher |  8a |  8b |  8c |  8d |
|--------------------|---|---|---|---|
| DMB | 0.30 ± 0.01 | 0.34 ± 0.03 | 0.030 ± 0.003 | 0.027 ± 0.002 |
| acetone | 5.42 ± 0.05 | 5.68 ± 0.05 | 0.0021 ± 0.0005 | <i>b</i> |
| acetic acid | 3.69 ± 0.48 | 2.21 ± 0.20 | 0.0039 ± 0.0005 | <i>b</i> |
| MeOH | (1.1 ± 0.4) + (64 ± 12)[MeOH] | (1.5 ± 0.6) + (58 ± 13)[MeOH] | < 0.001 ^c | <i>b</i> |
| O ₂ | 1.9 ± 0.2 | 1.62 ± 0.10 | 0.961 ± 0.045 | 0.96 ± 0.05 |
| CCl ₄ | 1.1 ± 0.1 | 1.2 ± 0.1 | 0.29 ± 0.03 | 0.35 ± 0.03 |
| HSiEt ₃ | < 0.0001 | < 0.0004 ^d | < 0.0004 ^d | <i>b</i> |

^a From polynomial least-squares fitting of k_{decay} vs [Q] data according to eqs 7 or 8. Errors are quoted as $\pm 2\sigma$. ^b Not determined. ^c Addition of up to 1.7 M MeOH had no effect on the lifetime in deoxygenated solution. ^d Addition of up to 4 M HSiEt₃ had no effect on the lifetime in deoxygenated solution.

nucleophilic quenching of **8d** was not investigated, the similarities in the rate constants for quenching by DMB, oxygen, and CCl₄ to those for **8c** provides reasonably compelling support for its assignment. Again, the alternative assignment of these transients to diphenyl- or dimethylgermylene can be ruled out by their lack of reactivity toward triethylsilane and/or chloroform; furthermore, the product studies indicate that their yields relative to those of **8c,d** are too low (when the differences in extinction coefficient are factored in) for them to dominate the observed transient absorption spectra.



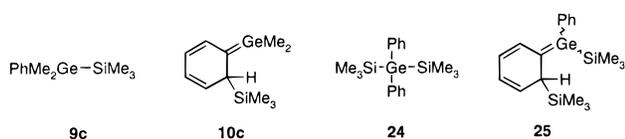
Attempts to obtain direct evidence for germylene formation from **7b,c** by laser flash photolysis have been

unsuccessful in both cases. Flash photolysis of **7b** in hexane containing 0.1 M MeOH, to shorten the lifetime of the (1-sila)hexatriene **8b** to <100 ns, afforded a transient absorption spectrum assignable to only $\text{Ph}_3\text{Si}^\cdot$. The long wavelength absorption band in the spectrum of the radical^{8,41} is expected to overlap with that due to dimethylgermylene, yet the decay kinetics in this monitoring wavelength range were identical to those measured at the maximum of the short wavelength absorption band of the radical at ~330 nm. Furthermore, addition of triethylsilane or *n*-bromohexane had no effect on the lifetime at either wavelength. Since product studies indicate that the yield of $\text{Me}_2\text{Ge}^\cdot$ from **7b** is in fact fairly high (vide supra), our failure to detect the germylene by flash photolysis is presumably due to its low expected extinction coefficient compared to that of the radical. Similar results were obtained in flash photolysis experiments with **7c** in methanolic hexane solution.

Steady state photolysis of a hexane solution of **7b** containing 0.5 M DMB and up to 4 M triethylsilane led to the formation of no new products and no reduction in the yield of **13_{Me}** relative to that of **12_{Si}** compared to that obtained in the absence of silane. This is surprising, since $\text{Me}_2\text{Ge}^\cdot$ has been reported to be only ~5 times less reactive toward hydrosilanes than DMB on the basis of time-resolved quenching experiments using permethylcyclopolygermane precursors ($k_{\text{Et}_3\text{SiH}} \approx 4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$).^{36,37,44} We do not understand the reasons for this, although it should be pointed out that the published kinetic results were not actually accompanied by supporting product studies.

It is interesting to note that the trends in the absolute reactivity of (1-germa)hexatriene **8c** toward O₂, CCl₄, DMB, and MeOH are very similar to those reported by Mochida and co-workers for $\text{Me}_2\text{Ge}^\cdot$, using permethylcyclopolygermanes as germylene precursors.^{37,44} We believe that these unanticipated similarities have led to erroneous assignments in some of the time-resolved studies of $\text{Me}_2\text{Ge}^\cdot$ and $\text{Ph}_2\text{Ge}^\cdot$ in solution which have been reported, in particular, those that have employed arylgermasilanes (e.g., **9c**^{31,32}) or aryl(disila)germanes (e.g., **24**³⁸) as germylene precursors. While steady state

trapping experiments clearly demonstrate that in both cases Me_2Ge : and Ph_2Ge : (respectively) are the major products of photolysis of these compounds in solution, they also show that the corresponding (1-germa)hexatriene derivatives are formed as well in significant yields. Flash photolysis of **9c** and **24** was reported to lead to the formation of transients absorbing in the 420–460 nm region, which were assigned to the germynes on the basis of their absorption maxima, the fact that in the absence of trapping agents they decay with second-order kinetics (consistent with dimerization to the corresponding digermene, whose second-order growth was also observed), and on the basis of absolute rate constants for reaction with reagents such as O_2 , DMB, CCl_4 , MeOH, and Et_3SiH . However, several of these rate constants (in particular, those for reaction with Et_3SiH) are in clear disagreement with those determined using other Me_2Ge :^{36,37,45} and Ph_2Ge :³⁶ precursors. On the basis of what we now know of the effects of substituents on the UV spectra and reactivity of transient silenes and germenes of homologous structure in solution,^{19,28,29,47–49} information that was not available at the time of the original studies, the data reported are more in line with those expected for the (1-germa)hexatriene analogues **10c** and **25**, respectively.

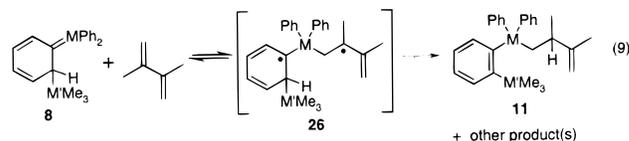


Comparison of the Reactivities of the Si=C and Ge=C Bonds in 8a–d. As mentioned earlier, the (1-sila)hexatriene derivatives **8a,b** are roughly 3 orders of magnitude more reactive than the germanium analogues **8c,d** toward methanol, acetic acid, and acetone (Table 1), a difference that is also mirrored in the simpler $\text{M}=\text{C}$ derivatives **23a,b**.²⁹ Both silenes and germenes react with alcohols (and probably acetic acid as well⁵⁰) via a mechanism involving initial complexation of the nucleophile at the heteroatom, followed by proton transfer.^{7,26,51,52} In the case of alcohols, the proton-transfer step occurs by two competing mechanisms, one involving unimolecular migration of the proton from oxygen to carbon and one involving catalysis by a second molecule of alcohol. Kinetically, the result of this is a mixed first- and second-order dependence of the silene/germene decay rate constant on alcohol concentration.^{7,26} The much lower reactivity of germenes compared to silenes toward nucleophiles can be explained as due primarily to the higher electronegativity of germanium relative to silicon, which leads to a less polar $\text{M}=\text{C}$ bond.^{28,29} This has the effect of slowing down the initial complexation step of these reactions and, because the complex is weaker, of reduc-

ing the rate at which it collapses to product by intramolecular proton transfer relative to reverting to starting materials.

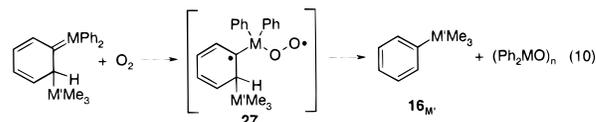
On the other hand, the reactivities of these compounds toward the diene, oxygen, and carbon tetrachloride are much less dependent on the identity of the group 14 heteroatom than is the case with nucleophilic quenchers. These three reagents do not react with silene **23a** at measurable rates in solution ($k \leq 10^6 \text{ M}^{-1} \text{ s}^{-1}$),⁵³ from which it can be concluded that their unusually high reactivity toward **8a,b** is due to the unique structure of the (1-sila)hexatriene system, which appears to accentuate reactivity (compared to simpler metallaethene systems) via biradical or biradicaloid mechanisms.¹⁹

The reaction of simple silenes and germenes with aliphatic dienes proceeds nonconcertedly, generally to yield a mixture of ene-, [2+2]-, and [4+2]-cycloaddition products.^{54–58} In contrast, the reaction of **8a** with DMB proceeds largely via ene-addition, although there is at least one other minor product formed in yields that are too low to allow isolation.¹⁹ The same is true of **8b–d**, according to GC/MS analysis of the reaction mixtures. We thus conclude that the reaction of dienes with **8** is also nonconcerted, most likely involving the biradical intermediate (**26**) shown in eq 9. The enhanced reactiv-



ity of **8** compared to simpler silenes and germenes presumably results from the facts that the initial step involves formation of a biradical with significantly greater resonance stabilization and that collapse of the biradical to the ene-adduct **11** enjoys an additional driving force due to aromatization. In this reaction, the germanium analogues **8c,d** are roughly 10 times less reactive than the silicon analogues **8a,b**.

Reaction of oxygen with aryldisilane-derived 1-(sila)hexatrienes such as **10a** and **8a** proceeds with bimolecular rate constants on the order of $10^9 \text{ M}^{-1} \text{ s}^{-1}$ and yields phenyltrimethylsilane (**16_{Si}**) and silanone oligomers (eq 9; $\text{M} = \text{M}' = \text{Si}$).¹⁹ The reaction presumably must proceed via a triplet biradical intermediate (**27**) such as that shown in eq 10, although the mechanism



for collapse of the biradical to the observed products is not well understood. It is interesting to note that the products correspond formally to those of R_2Si : extrusion

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from the disilane. Similar products are known to be formed upon reaction of silenes of this type with dimethyl sulfoxide.^{19,59} To verify that quenching of the 480–490 nm transients from flash photolysis of **7b** and **7c** with oxygen results in the same chemistry (and to provide further evidence consistent with their assignment), the two germasilanes were photolyzed in oxygen-saturated cyclohexane solution. As expected, photolysis of **7b** under these conditions led to the formation of phenyltrimethylgermane (**16Ge**, 7%), a product that is *not* formed in the absence of oxygen. Similarly, photolysis of **7c** under these conditions led to an enhancement in the yield of **16Si**, relative to that obtained in experiments in nitrogen-saturated solution.

Presumably, reaction of **8** with CCl₄ also proceeds via a radical mechanism, which would explain the similar reactivities of **8a,b** and **8c,d**, as well as the fact that simpler silenes and germenes such as **23a,b** show much lower reactivity toward this reagent. It seems most likely that the reaction is initiated by electron transfer, on the basis that quenching of **8a–d** by CCl₄ is at least 100 times faster than by chloroform. The mechanistic details are extremely difficult to ascertain, because CCl₄ also reacts rapidly with the excited singlet states of aryl-disilanes (including **7a**) by electron transfer, which ultimately results in Si–Si bond cleavage and the formation of the corresponding chlorosilanes.¹⁹ Similar behavior can be expected for **7b–d**.

Summary and Conclusions

The direct irradiation in solution of arylgermasilanes and -digermanes of the general structure Ph₃MM'Me₃ (**7b–d**) leads mainly to M–M' bond homolysis, at least partially via the lowest excited triplet state which is produced by intersystem crossing from the excited singlet state manifold in competition with the formation of a mixture of germylene, silene, and germene reactive intermediates. The latter are formed in similar yields and can be trapped by aliphatic dienes. This same general behavior has been reported previously for other arylgermasilanes and -digermanes,^{30–32} as well as aryl-disilagermanes³⁸ and aryltrigermanes.^{36,45} As with the disilane analogue **7a**, flash photolysis of **7b–d** results in the formation of strong transient absorptions due to arylsilyl or arylgermyl radicals ($\lambda_{\max} = 330\text{--}335$ nm), superimposed on absorptions due to a second transient species which absorbs at longer wavelengths ($\lambda_{\max} = 480\text{--}490$ nm).

In the case of Ph₃SiGeMe₃ (**7b**), this transient reacts with MeOH, AcOH, acetone, DMB, O₂, and CCl₄ in hydrocarbon solution with rate constants nearly identical to that of the (1-sila)hexatriene (**8a**) observed under similar conditions from Ph₃SiSiMe₃ (**7a**) and can thus be identified as the (1-sila)hexatriene derivative **8b**. Neither the absorption maximum nor the reactivity of the transient is consistent with a possible alternative assignment to Me₂Ge₂, on the basis of the various studies of this transient germylene that have been previously reported. This is not unexpected, since product studies indicate that the germylene is formed in only ca. twice the yield of **8b**, and the extinction

coefficient of the long wavelength n,p absorption band of the germylene can be expected to be at least an order of magnitude lower than that of the π,π^* absorption band of the silene.⁴⁶

The long wavelength transient from flash photolysis of Ph₃GeSiMe₃ (**7c**) absorbs with $\lambda_{\max} \approx 480$ nm and reacts with nucleophilic quenchers (HOAc, MeOH, and acetone) with rate constants that are on the order of 10³ lower than those for reaction of **8a,b** with the same reagents. Much higher reactivity is observed toward O₂, CCl₄, and dienes, with absolute rate constants that are only 2–10 times lower than the corresponding values for reaction of **8a,b**. The transient has been assigned to the (1-germa)hexatriene **8c** on the basis of these data. Again, an alternative assignment to Ph₂Ge₂, which product studies suggest is formed in roughly twice the yield of **8c**, can be ruled out on the basis of the extinction coefficient arguments discussed earlier, its low reactivity toward triethylsilane and chloroform, and the fact that Ph₂Ge₂ has been reported to absorb at somewhat shorter wavelengths ($\lambda_{\max} 445\text{--}460$ nm^{30,35,36,38,60}) than the transient observed from **8c**. A transient with the same absorption maximum and identical reactivity toward O₂, CCl₄, and DMB is observed in the case of the digermane **7d** and is identified as (1-germa)-hexatriene **8d**.

The 1000-fold lower reactivity of **8c,d** compared to **8a,b** toward oxygen-containing nucleophilic trapping agents such as alcohols, carboxylic acids, and ketones parallels the differences reported previously for 1,1-diphenylsilene (**23a**) and 1,1-diphenylgermene (**23b**).^{28,29} Much smaller differences in reaction rate are observed for DMB, O₂, and CCl₄, reagents that are normally relatively unreactive toward either silenes or germenes of simpler structure (e.g., **23a,b**). This unusually high, relatively indiscriminate reactivity is presumably due to the presence of the cyclohexadienyl substituent at the metallaene carbon atoms in **8a–d**, which would clearly be expected to promote reactions that proceed through radical or biradical intermediates.

Experimental Section

¹H and ¹³C NMR spectra were recorded on Bruker AC200 or DRX500 NMR spectrometers in deuterated chloroform solution and are referenced to tetramethylsilane. Ultraviolet absorption spectra were recorded on Hewlett-Packard HP8451 or Perkin-Elmer Lambda 9 spectrometers. Low-resolution mass spectra and GC/MS analyses were determined using a Hewlett-Packard 5890 gas chromatograph equipped with a HP-5971A mass selective detector and a DB-5 fused silica capillary column (30m × 0.25 mm; Chromatographic Specialties, Inc.). High-resolution desorption electron impact (DEI) mass spectra and exact masses were recorded on a VGH ZABE mass spectrometer. Exact masses employed a mass of 12.000000 for carbon. Infrared spectra were recorded on a BioRad FTS-40 FTIR spectrometer and are reported in wavenumbers (cm⁻¹).

Analytical gas chromatographic analyses were carried out by GC/MS or using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector, a Hewlett-Packard 3396A recording integrator, conventional heated splitless injector, and a DB-1 fused silica capillary column (15 m × 0.20 mm; Chromatographic Specialties, Inc.). Semi-preparative GC separations employed a Varian 3300 gas chromatograph equipped with a thermal conductivity detector and a 6' × 0.25" stainless steel OV-101 packed column

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(Chromatographic Specialties). Radial chromatographic separations employed a Chromatotron (Harrison Research, Inc.), 2- or 4-mm silica gel 60 thick-layer plates, and hexane/ethyl acetate mixtures as eluant.

Hexane (BDH Omnisolv) was used as received without additional purification or drying. Methanol, 2,3-dimethyl-1,3-butadiene, acetone (HPLC grade), acetic acid, chloroform, and carbon tetrachloride were used as received from Aldrich Chemical Co. Deuterated materials were used as received from Cambridge Isotope Labs. Compounds **7b–d** were prepared and purified as previously reported.⁶¹

Solutions of **7b–d** (0.1 g, 3.66×10^{-4} mol) in hexane (15 mL) containing 2,3-dimethyl-1,3-butadiene (0.5 M) were placed in quartz tubes, which were then sealed with rubber septa and deoxygenated with a stream of dry argon. The samples were then photolyzed for 1 h in a Rayonet reactor equipped with a merry-go-round and six RPR2537 lamps, with periodic monitoring of the course of the photolysis by GC. Methyltriphenylsilane (**12_{Si}**), triphenylsilane (**14_{Si}**), trimethylphenylsilane (**16_{Si}**), methyltriphenylgermane (**12_{Ge}**), triphenylgermane (**14_{Ge}**), and trimethylphenylgermane (**16_{Ge}**) were identified by GC and/or GC/MS co-injection with authentic samples obtained from Aldrich Inc. or synthesized by known routes. The germylene-diene adducts **13_{Me}** and **13_{Ph}** were isolated by semipreparative GC, from the photolysis mixtures from **7b** and **7c**, respectively, after evaporation of the solvent and dissolution of the resulting colorless oils in a small amount of pentane. The two compounds were identified by comparison of their ¹H NMR and mass spectra to previously reported data.³² The (1-metalla)hexatriene adducts **11b,c** were isolated by semipreparative GC and identified on the basis of the spectroscopic data listed below. Adduct **11d** (from **7d**) was identified on the basis of GC retention time and mass spectral comparisons to **11a–c**.

1-(Trimethylgermyl)-2-((2,3-dimethyl-1-buten-4-yl)-diphenylsilyl)benzene (11b). ¹H NMR (CD₂Cl₂): δ 0.06 (s, 9H), 0.84 (d, 3H), 1.46 (m, 2H), 1.63 (s, 3H), 2.48 (m, 1H), 4.54 (s, 1H), 4.58 (s, 1H), 7.21–7.66 (m, 14H). ¹³C NMR (CD₂Cl₂; quaternary carbons not resolved): δ 2.12, 19.07, 22.23, 22.85, 37.90, 108.74, 127.47, 128.28, 129.09, 129.73, 134.47, 135.96, 136.41. MS (EI): *m/z* (I) 460 (1), 445 (4), 377 (20), 367 (15), 341 (15), 299 (15), 259 (50), 222 (100), 197 (50), 181 (50), 135 (25), 105 (25). Exact mass: calcd for (M – 83) C₂₁H₂₃⁷⁰GeSi, 373.0811; found 373.0795.

1-(Trimethylsilyl)-2-((2,3-dimethyl-1-buten-4-yl)-diphenylgermyl)benzene (11c). ¹H NMR: δ 0.02 (s, 9H), 0.92 (d, 3H), 1.55 (m, 2H), 1.64 (s, 3H), 4.56 (m, 2H), 7.32–7.51 (m, 14H). MS: *m/z* (I) 460 (5), 445 (1), 377 (100), 362 (5), 347 (5), 299 (30), 243 (20), 227 (30), 195 (20), 181 (20), 151 (40), 135 (35), 105 (10), 73 (20). Exact mass: calcd for (M – 83) C₂₁H₂₃⁷⁰GeSi, 373.0811; found 373.0793.

1-(Trimethylgermyl)-2-((2,3-dimethyl-1-buten-4-yl)-diphenylgermyl)benzene (11d). MS (EI): *m/z* (I) 489 (1), 421 (100), 407 (10), 389 (10), 343 (25), 310 (20), 268 (20), 243, (50), 227 (50), 181 (50), 151 (80), 119 (25), 91 (20).

Solutions of **7b–d** (0.1 g, 3.66×10^{-4} mol) in hexane (15 mL) containing *n*-decanol (0.1 M) were photolyzed as described above and monitored by GC, which revealed the formation of *n*-decyloxytrimethylsilane (**18_{Si}**) or *n*-decyloxytrimethylgermane (**18_{Ge}**), along with other products. Compounds **18** were identified by GC/MS and by GC co-injection with authentic samples, which were synthesized under a nitrogen atmosphere using dry oxygen-free solvents, as follows.

For the synthesis of **18_{Si}**, a solution of trimethylchlorosilane (4 g, 36.9 mmol) in anhydrous ether was added dropwise to a stirred solution of triethylamine (7.5 g, 73.8 mmol) and *n*-decanol (5.8 g, 36.9 mmol) in anhydrous ether (10 mL), which were contained in a 250 mL round-bottom flask fitted with magnetic stirrer, condenser, dropping funnel, nitrogen inlet, and ice bath. A colorless precipitate of triethylamine hydrochloride was formed immediately. The mixture was stirred for 1 h and then filtered, and the solvent was removed under vacuum to afford a slightly yellow liquid. Atmospheric distillation of the material afforded 1-trimethylsiloxydecane (**18_{Si}**) as a colorless liquid (bp 234–240 °C; 2.87 g, 12.5 mmol, 34%). Compound **18_{Ge}** was synthesized in similar fashion from trimethylgermanium chloride (4.1 g, 26.2 mmol), *n*-decanol (4.1 g, 26.2 mmol), and triethylamine (5.3 g, 52.4 mmol). Distillation under reduced pressure afforded 1-trimethylgermoxydecane (**18_{Ge}**) as a colorless liquid (bp 130 °C (20 mm); 1.24 g, 4.5 mmol, 19%). The two compounds exhibited the following NMR and mass spectral data.

1-Trimethylsiloxydecane (18_{Si}). ¹H NMR: δ 0.11 (s, 9H), 0.88 (t, 3H, *J* = 7.0 Hz), 1.27 (bd s, 14H), 1.53 (t, 2H, *J* = 6.5 Hz), 3.57 (t, 2H, *J* = 6.7 Hz). ¹³C NMR: δ –0.13, 14.5, 23.1, 26.2, 29.7, 29.8, 30.0, 30.0, 32.3, 33.1, 63.1. ²⁹Si NMR: δ 17.1. MS (EI): *m/z* (I) 230 (5), 215 (100), 199 (5), 187 (5), 157 (10), 143 (10), 129 (10), 115 (20), 103 (30), 75 (75), 73 (50).

1-Trimethylgermoxydecane (18_{Ge}). ¹H NMR: δ 0.39 (s, 9H), 0.89 (3H, t, *J* = 6.9 Hz), 1.27 (bd s, 14H), 1.53 (t, 2H, *J* = 6.9 Hz), 3.55 (2H, t, *J* = 6.9 Hz). ¹³C NMR: δ 0.48, 14.5, 23.1, 26.4, 29.7, 29.8, 30.0, 30.1, 33.2, 34.0, 64.9. MS (EI): *m/z* (I) 276 (5), 261 (10), 231 (5), 203 (5), 189 (5), 173 (7), 149 (75), 119 (100), 105 (30), 89 (30), 75 (5).

Nanosecond laser flash photolysis experiments employed the pulses (248 nm; ca. 16 ns; ca. 50 mJ) from a Lambda-Physik Compex 120 excimer laser filled with F₂/Kr/He mixtures and a microcomputer-controlled detection system.⁶² Solutions were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was ca. 0.7 (4.4×10^{-3} M) and were flowed continuously through a 3 × 7 mm Suprasil flow cell connected to a calibrated 100 mL reservoir. Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple, which was inserted directly into the flow cell, and are accurate to within 0.1 °C. 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 (6–15 points, depending on whether the plots were linear or curved), 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.

Acknowledgment. We wish to thank D. Hughes for his assistance with high-resolution NMR spectra, the McMaster Regional Centre for Mass Spectrometry for high-resolution mass spectra and exact mass determinations, and Professors Kunio Mochida and Peter Gaspar for helpful comments. The financial support of the Natural Sciences and Engineering Research Council (NSERC) of Canada (to W.J.L.) and the Robert Welch Foundation (to K.H.P.) is also gratefully acknowledged.

OM000174P

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