# Time-resolved spectroscopic studies of the photochemistry of some diphenylgermylene (Ph<sub>2</sub>Ge:) precursors<sup>1</sup>

Cameron R. Harrington, William J. Leigh, Bryan K. Chan, Peter P. Gaspar, and Dong Zhou

Abstract: The photochemistry of diphenylbis(trimethylsilyl)germane (2a) and 1,4-dihydro-5-methyl-1,2,3,4,9,9hexaphenyl-1.4-germanonaphthalene (11) has been studied in solution by steady-state and laser flash photolysis methods with a view to detecting the transient germylene derivative diphenylgermylene (Ph<sub>2</sub>Ge), which has previously been shown to be the major product of photolysis of 2a and a closely related derivative of 11. Steady-state trapping experiments confirm the formation of  $Ph_2Ge$  as the major germanium containing primary product in both cases; with 2a, the results indicate that other transient species are also formed in minor yields, including phenyl(trimethylsilyl)germylene (Ph(TMS)Ge, ca. 6%) and diphenyl(trimethylsilyl)germyl radicals (Ph<sub>2</sub>(TMS)Ge,  $\geq 15\%$ ). Laser flash photolysis of **2a** in deoxygenated hexane solution yields a complex mixture of overlapping transient absorptions, which is shown to be comprised of  $Ph_2Ge$ , tetraphenyldigermene (15) and its oligomerization products, and another species with spectral characteristics similar to the Ph2(TMS)Ge radical. The latter has been independently generated by hydrogen abstraction from diphenyl(trimethylsilyl)germane by tert-butoxyl radicals. Compound 11 extrudes Ph<sub>2</sub>Ge more cleanly and efficiently upon photolysis in solution, yet laser flash photolysis affords excited triplet and triplet-derived species as the only detectable transient products; interpretation of the results for this compound is made difficult by its slow thermal decomposition to 5-methyl-1.2,3,4-tetraphenylnaphthalene. It is concluded that in spite of the fact that both 2a and 11 afford Ph<sub>2</sub>Ge in high yield upon photolysis, they are poor precursors for study of the species in solution by timeresolved UV-vis methods, owing to the formation of other, more strongly absorbing transient products than Ph<sub>2</sub>Ge, whose lowest energy absorption is characteristically weak.

Key words: germylene, germyl radical, flash photolysis, disilylgermane, photochemistry.

Résumé : Afin d'essayer de détecter le dérivé germylène transitoire, diméthylgermylène (Ph2Ge), qui avait été reconnu antérieurement comme le produit principal de la photolyse du produit 2a et de son dérivé apparenté 11, on a étudié la photochimie du diphénylbis(triméthylsilyl)germane (2a) et du 1,4-dihydro-5-méthyl-1,2,3,4,9,9-hexaphényl-1,4germanonaphtalène (11) en solution, par les méthodes de l'état stationnaire et de la photolyse éclair au laser. Les expériences de piégeage de l'état stationnaire confirment dans les deux cas la formation du Ph<sub>2</sub>Ge comme produit primaire principal contenant du germanium; avec le produit 2a, les résultats indiquent que d'autres espèces transitoires se forment aussi, avec des rendements mineurs, dont les radicaux phényl(triméthylsilyl)germylène (Ph(TMS)Ge; rendement d'environ 6 %) et diphényl(triméthylsilyl)germyle (Ph<sub>2</sub>(TMS)Ge; rendement supérieur à 15 %). La photolyse éclair au laser du composé 2a en solution d'hexane désoxygéné mène à la formation d'un mélange complexe d'absorptions transitoires qui se superposent; il a été démontré qu'elles comprennent le Ph<sub>2</sub>Ge, le tétraphényldigermène (15) et ses produits d'oligomérisation ainsi qu'une autre espèce de caractéristiques spectrales similaires au radical Ph<sub>2</sub>(TMS)Ge. Ce dernier a été généré de manière indépendante par abstraction d'hydrogène par des radicaux tert-butoxyles à partir du diphényl(triméthylsilyl)germane. Par photolyse en solution, le composé 11 expulse le Ph<sub>2</sub>Ge d'une façon beaucoup plus propre et plus efficace, toutefois la photolyse éclair au laser ne fournit comme produits transitoires détectables que le triplet excité et diverses espèces qui en dérivent; l'interprétation des résultats relatifs à ce composé est rendue difficile par sa décomposition thermique lente en 5-méthyl-1,2,3,4-tétraphénylnaphtalène. On en conclut que, même si la photolyse des composés 2a et 11 mène dans les deux cas à la formation de Ph<sub>2</sub>Ge avec un rendement élevé, ils sont de pauvres précurseurs pour l'étude de ces espèces en solution par des méthodes UV-vis résolues dans le temps en raison de la formation d'autres produits transitoires qui absorbent plus fortement que le Ph2Ge dont la plus faible énergie d'absorption est normalement faible.

Received 9 March 2005. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on 22 October 2005.

<sup>1</sup>This article is part of a Special Issue dedicated to organic reaction mechanisms. <sup>2</sup>Corresponding author: (e-mail: leigh@mcmaster.ca).

**C.R. Harrington, W.J. Leigh,<sup>2</sup> B.K. Chan, P.P. Gaspar, and D. Zhou.** Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, ON L8S 4M1, Canada and Department of Chemistry, Washington University, St. Louis, MO 63130, USA.

Mots clés : germylène, radical germyle, photolyse éclair, disilylgermane, photochimie.

[Traduit par la Rédaction]

# Introduction

Since the report nearly 20 years ago by Ando et al. (1) of the UV spectra of several simple, photochemically generated germylene derivatives in hydrocarbon matrixes at low temperature, there have been a number of studies published on the direct detection and study of reactive diarylgermylenes (2-10) and dialkylgermylenes (6, 11-15) in solution by laser flash photolysis techniques. Most of these studies employed Group 14 catenates as photochemical precursors to these "heavy carbene" analogues, such as 1-3 in the case of diphenylgermylene (Ph<sub>2</sub>Ge). While steady-state trapping experiments showed that the germylene is the major transient photoproduct in each case, the results of laser photolysis experiments have been highly variable. For example, the UVvis absorption max of Ph2Ge has been reported to occur at various positions ranging from 445 to 630 nm, bracketing the value of  $\lambda_{max} = 466$  nm originally reported by Ando et al. (1) in a 3-methylpentane matrix at 77 K using benzogermanorbornadiene derivative 4 and disilylgermane 2a as germylene precursors. Thanks to the recent identification of a precursor that yields this reactive species quantitatively and in remarkably high quantum efficiency (5, eq. [1]), the UV spectrum of Ph<sub>2</sub>Ge in hydrocarbon solvents at room temperature has now been conclusively established (9), as have quantitative details of its reactivity toward dimerization (9) and a number of representative metallylene scavengers such as amines, carboxylic acids, halocarbons, Group 14 hydrides, dienes, alkenes, and alkynes (10). In hexane solution at room temperature, diphenylgermylene exhibits  $\lambda_{max}$  = 500 nm ( $\epsilon = 1650 \pm 390 \text{ (mol/L)}^{-1} \text{ cm}^{-1}$ ) and dimerizes at close to the diffusion-controlled rate to yield the transient 1,1,2,2-tetraphenyldigermene (Ph<sub>2</sub>Ge=GePh<sub>2</sub>,  $\lambda_{max}$  = 440 nm,  $\tau \sim 40 \,\mu s$ ) (9). None of the UV spectra previously assigned to  $Ph_2Ge$  — including that reported by Ando et al. in 3-MP



1325

matrices at 77 K (1, 16, 17) — match the one reported more recently in solution using **5** as the precursor.

One of the compounds employed by Ando et al. for the photogeneration of Ph2Ge - diphenylbis(trimethylsilyl)germane (2a) — has also been studied in fluid solution at room temperature by flash photolysis methods (2, 6). Photolysis of the compound in cyclohexane solution in the presence of 2,3-dimethyl-1,3-butadiene (DMB) was found to afford hexamethyldisilane (Si<sub>2</sub>Me<sub>6</sub>), trimethylphenylsilane (PhSiMe<sub>3</sub>), and the diene trapping product 5 as the only detectable products (eq. [2]) (6), while laser flash photolysis of the compound afforded a transient that decayed over several hundred microseconds and exhibited  $\lambda_{max} = 445$  nm (2), blue-shifted somewhat relative to the spectrum recorded for this compound in the earlier matrix experiments (1, 16). Absolute rate constants were determined for reaction of the species with various germylene scavengers, among them oxygen  $(1.02 \times 10^8 \text{ (mol/L)}^{-1} \text{ s}^{-1})$ , ethyldimethylsilane (k = 1.01 ×  $10^4 \text{ (mol/L)}^{-1} \text{ s}^{-1}$ , 1-bromo-2-methylpropane (k = 6.36 ×  $10^5 \text{ (mol/L)}^{-1} \text{ s}^{-1}$ ), and 2,3-dimethyl-1,3-butadiene (2.75 ×  $10^4 \text{ (mol/L)}^{-1} \text{ s}^{-1}$ ) (2). Like the UV-vis spectrum, the reactivity of the transient toward the various germylene scavengers examined is in poor agreement with that reported much later for  $Ph_2Ge$  using 5 as the precursor (9). It is noteworthy that photolysis of the dimesityl analogue of 2a (6) also affords the corresponding germylene (in this case dimesitylgermylene, Mes<sub>2</sub>Ge) quite cleanly, as shown by the results of steady-state trapping experiments, matrix photolysis experiments (1, 16), and laser flash photolysis experiments in solution (7). In this case, the transient spectrum observed (and assigned to Mes<sub>2</sub>Ge,  $\lambda_{max} \sim 550$  nm) in solution (7) matches that obtained in matrix experiments (1, 16) or in solution from other precursors (7, 9) quite closely.





Recently, we reported a study of the photochemistry of 1,1,1-trimethyl-2,2,2-triphenylsilagermane (7) in solution by steady-state and laser flash photolysis methods (18). This compound also yields  $Ph_2Ge$  as the major germanium containing photoproduct in solution, but it also affords significant yields of the conjugated germene derived from 1,3-trimethylsilyl migration (8) and free radicals owing to triplet-derived Ge—Si bond homolysis (eq. [3]), as revealed by the results of steady-state trapping experiments. Only 8

and triphenylgermyl radicals could be detected in laser flash photolysis experiments with the molecule, presumably because the absorption spectra of these transients are significantly more intense than that of Ph<sub>2</sub>Ge, whose lowest energy (n,p) electronic transition is characteristically weak. Furthermore, the lowest energy absorption band in the UV-vis spectrum of **8** ( $\lambda_{max} \sim 475$  nm) occurs at a similar position to the much weaker absorption band in the spectrum of the germylene ( $\lambda_{max} = 500$  nm) under similar conditions. We speculated that an analogous mixture of products might well be expected from photolysis of **2a** under similar conditions, and that the transient spectroscopic behavior reported earlier for this compound might thus be better explained in terms of the corresponding germene (**9**) and (or) the diphenyl(trimethylsilyl)germyl radical (**10**) (18).



In the present paper, we report the results of a reinvestigation of the photochemistry of **2a** in solution by steady-state and laser flash photolysis methods, with a view to providing a secure identification of the transient species observed in the earlier work with this compound, and to see whether discrete evidence for the formation of free Ph<sub>2</sub>Ge might be obtained. To aid in the interpretation of the results, germyl radical **10** has been generated by an independent route and its UV-vis spectrum and lifetime recorded under similar conditions to those employed for laser photolysis experiments with 2a. We have also synthesized an analogue (11) of the benzogermanonorbornadiene derivative originally studied by Ando et al. (4), and have studied its photochemistry using similar methods. This compound differs from 4 only in the presence of a methyl group situated on the benzannelated ring, which was included so as to facilitate the determination of its purity and the identification of products from photochemical and (or) thermal decomposition, as compounds of this type are known to exhibit pronounced thermal lability under quite mild conditions (19–22).



# **Results and discussion**

#### The photochemistry of Ph<sub>2</sub>Ge(SiMe<sub>3</sub>)<sub>2</sub> (2a)

The products of photolysis of 2a in the presence of DMB (see eq. [2]) were originally identified, and their yields established, from a preparative-scale photolysis experiment carried to 64% conversion (6). Because secondary photolysis of 5 can be expected to lead to its preferential loss from the reaction mixture over such extended photolysis times, we began the present study with an examination of the product mixture at much lower conversions. Thus, a deoxygenated 0.05 mol/L solution of **2a** in cyclohexane- $d_{12}$  containing 0.1 mol/L of the diene was irradiated with 254 nm light, monitoring the reaction periodically by (600 MHz) <sup>1</sup>H NMR spectroscopy over the 0%-16% conversion range. The NMR spectra of the photolysate showed discrete evidence for the formation of 5 and hexamethyldisilane (Si<sub>2</sub>Me<sub>6</sub>) in a ca. 1:1 ratio as the only detectable products. GC analysis of a similar photolysis in deoxygenated hexane solution (0.01 mol/L 2a, 0.03 mol/L DMB) also showed 5 to be the major product of the reaction, but allowed the additional detection of PhSiMe<sub>3</sub> in minor amounts ( $\leq 6\%$ ), along with another minor product that eluted shortly before 2a. The latter compound, which is formed in similar yield to PhSiMe<sub>3</sub>, was tentatively identified as 3,4-dimethyl-1-phenyl-1-trimethylsilylgermacyclopent-3-ene (12) on the basis of GC-MS evidence. The results of these experiments are summarized in eq. [4].



Interestingly, photolysis of a 0.05 mol/L solution of 2a in cyclohexane-d<sub>12</sub> containing methanol (MeOH, 0.5 mol/L) afforded Si<sub>2</sub>Me<sub>6</sub> and the Ph<sub>2</sub>Ge insertion product 13 as the major products, but the latter was formed in only ca. 60% yield relative to consumed 2a and in significantly lower yield than the coproduct of Ph<sub>2</sub>Ge extrusion, Si<sub>2</sub>Me<sub>6</sub>. The 0–0.5 ppm region of the spectra also contained singlets attributable to three additional minor products, whose resonances integrated to 10:13:7; the total intensity of the three singlets owing to these products was ca. 30% relative to that of the singlet owing to Si<sub>2</sub>Me<sub>6</sub>. The most minor of these products was identified by <sup>1</sup>H NMR spectroscopy and GC as disilyldigermane 14, by spiking the mixture with an authentic sample of the compound; the other two were not identified. The results of these experiments are summarized in eq. [5].

Taken together, these results indicate that while extrusion of  $Ph_2Ge$  is the dominant photoreaction of **2a**, accounting for ca. 60% of the photochemistry, other minor processes occur as well. One of these is assigned to the alternate germylene extrusion pathway, yielding Ph(TMS)Ge and



+  $Si_2Me_6$  (1.17:1 relative to **13**)

PhSiMe<sub>3</sub> in about 6% chemical yield. Another is Si-Ge bond homolysis to yield the trimethylsilyl and diphenyl(trimethylsilyl)germyl radicals, as evidenced by the formation of minor amounts of digermane 14 in the photolysis in the presence of MeOH. This process constitutes at least 15% of the reactive excited-state decay processes of the molecule, based on the observed yield of 14 and the assumption that 50% of the Ph2(TMS)Ge radicals produced will decay by recombination with trimethylsilyl radical, regenerating 2a. Interestingly, 14 is not formed in the diene scavenging experiment, and the complete absence of additional SiMe<sub>3</sub> resonances in the NMR spectrum of this photolysis mixture indicates that the reason is not that the Ph<sub>2</sub>(TMS)Ge radical is efficiently scavenged by the diene. A more likely mechanism by which the diene suppresses the formation of free radicals is triplet quenching, since it is known that the formation of radicals in the photolysis of aryldisilanes, arylgermasilanes, and aryldigermanes derives largely from the triplet state, and their formation can be quenched to at least some extent by added diene (18, 23, 24).

Laser flash photolysis experiments with 2a employed flowed, deoxygenated  $1.3 \times 10^{-4}$  mol/L solutions of the compound in anhydrous hexane, and used the pulses from a KrF excimer laser (248 nm, ~25 ns, ~100 mJ) for excitation. As reported previously (2), laser photolysis of the compound affords strong transient absorptions throughout the 300-600 nm region of the spectrum, which decay over several hundred microseconds with complex kinetics. Figure 1 shows transient spectra recorded at selected time intervals over a ca. 350 µs time window after excitation in the absence and presence of 3 mmol/L acetic acid (AcOH). The spectra in the absence of acid were collected with a view to reproducing the originally reported conditions as closely as possible, while those in the presence of acid were intended to reveal those transient absorptions that remain behind when Ph2Ge and its oligomerization products are removed from the mixture by trapping with AcOH, a potent germylene scavenger (9, 10). The main (gross) effects of the carboxylic acid are a marked reduction in the intensities of the signals observed throughout the spectrum, and simplification of the complex transient absorptions that arise below ca. 340 nm. In the absence of AcOH (Fig. 1a), the spectrum exhibits a band at  $\lambda_{max} = 300$  nm during the earliest time window monitored, which evolves into a band with  $\lambda_{max} \sim$ 310 nm after ca. 25 µs; only the latter is evident in the region below 340 nm in the presence of the carboxylic acid (Fig. 1b). Addition of the acid also reduces the intensity of the long wavelength absorption band centered at  $\lambda_{max}$  ~ 445 nm, and markedly reduces the complexity of the tran-

**Fig. 1.** Transient absorption spectra from laser flash photolysis of a flowed, deoxygenated solution of **2a**  $(1.3 \times 10^{-4} \text{ mol/L})$  in anhydrous hexane containing (*a*) 0 mmol/L of AcOH and (*b*) 3 mmol/L AcOH, recorded under identical conditions, 0.64–2.56 µs ( $\bigcirc$ ), 24–39 µs ( $\square$ ), and 324–325 µs ( $\triangle$ ) after the pulse. Transient decay traces recorded at a monitoring wavelength of 440 nm are shown as inserts.



sient decay profile at this wavelength, which decays with multiexponential kinetics in the absence of acid (see inset, Fig. 1*a*). In the presence of 3 mmol/L AcOH the long wavelength absorption decays with clean second-order kinetics (see inset, Fig. 1*b*) and a rate coefficient of  $k_{decay}/\epsilon = (7.4 \pm 0.2) \times 10^5$  cm<sup>-1</sup> s<sup>-1</sup> ( $r^2 = 0.987$ ). The decay kinetics at 310 nm (not shown) are similar to those at 440 nm, suggesting that the two absorption bands in the spectrum of Fig. 1*b* belong to the same (as yet unidentified) transient species. It can thus be concluded that the early (0.64–2.56 µs) spectrum of Fig. 1*a* is the sum of the spectra of at least two transient species of which all but one is eliminated in the presence of 3 mmol/L AcOH.

AcOH is known to react with Ph<sub>2</sub>Ge irreversibly, with a rate constant of  $3.9 \times 10^9 \text{ (mol/L)}^{-1} \text{ s}^{-1}$  (9). Thus, a concentration of 3 mmol/L is sufficient to reduce the lifetime of Ph<sub>2</sub>Ge to <100 ns and more or less completely suppress its dimerization to tetraphenyldigermene (**15**), the main mode of decay of the germylene in the absence of scavengers (see eq. [6]) (9). In the absence of scavengers, the concentration

of 15 reaches a maximum in the first ca. 1 µs after the excitation pulse, and then decays over several tens of microseconds (9). We thus attribute that portion of the transient spectrum of Fig. 1*a* that is eliminated in the presence of AcOH to 15 ( $\lambda_{max} = 300$ , 440 nm (9)), formed by dimerization of Ph<sub>2</sub>Ge, and its oligomerization product(s). The long wavelength absorption band in the spectrum of 15 is almost exactly coincident with that of the longer lived (nonquenchable) species that was erroneously identified as owing to Ph<sub>2</sub>Ge in the original work (2).



Direct evidence for the formation of Ph<sub>2</sub>Ge from 2a was obtained by examination of the transient spectroscopic behavior over shorter timescales. Figure 2 shows transient spectra recorded at selected time intervals within ca. 1 µs after excitation, along with representative transient absorption profiles recorded at 510 and 440 nm. As can be seen from the data, the long wavelength absorption band in the transient spectrum from 2a is centered at  $\lambda_{max} \sim 465$  nm during the first ca. 100 ns after excitation, and appears to shift to  $\lambda_{max} \sim$  445 nm (its position in the spectra of Fig. 1) during the next ~900 ns. Inspection of the transient absorption profile at 440 nm reveals a slight increase in signal strength at this wavelength over this early time period, indicative of the delayed formation of a species that is not present (or at least present in lower concentration) immediately after the ca. 25 ns laser pulse. Thus, the apparent shift in the position of the long wavelength transient absorption during the first microsecond after excitation can be understood as owing to the superposition of three distinct transient absorptions that each evolve differently over this timescale: one that decays almost completely (465 nm <  $\lambda_{max}$  < 550 nm), one that grows in (400 nm <  $\lambda_{max}$  < 460 nm), and one that is essentially nondecaying ( $\lambda_{max} \sim 445$  nm, see Fig. 1b). This behavior is consistent with the initial formation of Ph<sub>2</sub>Ge ( $\lambda_{max}$  = 500 nm (9)), which decays over 1 to  $2 \,\mu s$  by dimerization to yield 15 ( $\lambda_{max}$  = 440 nm (9)). The timescale over which these changes occur correlates almost precisely with that found in our previous study of these species, generated by laser photolysis of 5 (9). The transient decay profiles shown in Fig. 2 bear only qualitative similarities to those previously obtained from 5 (9), however, owing to the presence of the third transient species, which absorbs relative strongly over the same range of the spectrum, and whose decay proceeds over a much longer timescale.

Inspection of the transient absorption profiles over the short timescale as AcOH is added to the solution provides somewhat clearer evidence for the presence of  $Ph_2Ge$  and its dimerization product in the transient mixture. Figures 3a and 3b show a series of decay profiles recorded at the two wavelengths in the presence of 0, 0.1, and 2.0 mmol/L of added carboxylic acid, demonstrating quite clearly that a signifi-

**Fig. 2.** (*a*) Transient absorption spectra from laser flash photolysis of a flowed, deoxygenated solution of **2a**  $(1.3 \times 10^{-4} \text{ mol/L})$  in anhydrous hexane, 30–80 ns ( $\bigcirc$ ) and 1.0–1.2 µs ( $\square$ ) after the pulse. The dashed line is the difference between the early and late spectrum. (*b*) Transient absorption profiles recorded at 440 nm ( $\bigcirc$ ) and 510 nm ( $\square$ ).



cant portion of the signal at 510 nm is quenched by the reagent, concomitant with a reduction in the yield of a transient absorbing at 440 nm. Nonlinear least-squares analysis of the initial rapidly decaying portion of the 510 nm decay profiles at several AcOH concentrations as a single exponential decay (with the more slowly decaying residual absorption treated as nondecaying) afforded quite reasonable fits; the resulting pseudo-first-order decay rate constants  $(k_{decay})$  are plotted in Fig. 3c vs. AcOH concentration. Linear least-squares analysis of these data according to eq. [7], where  $k_0$  is the effective pseudo-first-order decay rate constant at [AcOH] = 0 and  $k_{AcOH}$  is the bimolecular rate constant for scavenging by the carboxylic acid, affords a slope of  $k_{\text{ACOH}} = (5.5 \pm 0.5) \times 10^9 \text{ (mol/L)}^{-1} \text{ s}^{-1}$ , in excellent agreement with the value reported by us earlier for the O-H insertion reaction of Ph<sub>2</sub>Ge with AcOH ( $k_{AcOH} = 3.9 \times 10^9 \text{ (mol/L)}^{-1} \text{ s}^{-1} (9)$ ). Figure 3b also shows the result of subtracting the decay trace at 440 nm in the presence of 2.0 mmol/L AcOH (where formation of 15 should be more or less completely suppressed) from that recorded in the ab-

**Fig. 3.** Transient decay traces recorded with a deoxygenated anhydrous hexane solution of **2a** at (*a*) 510 nm and (*b*) 440 nm in the presence of 0 mmol/L AcOH ( $\bigcirc$ ), 0.1 mmol/L AcOH ( $\square$ ), and 2.0 mmol/L AcOH ( $\triangle$ ). The grey trace in (*b*) is the difference between the 0 and 2.0 mmol/L traces. (*c*) Plot of the rate constant for the initial rapid decay at 510 nm ( $k_{decay}$ ) vs. [AcOH] over the 0.3–2.0 mmol/L concentration range.



1329

sence of scavenger. This is also in good agreement with the growth-decay profile for 15 that is observed using 5 as the germylene precursor (9).

$$[7] k_{decay} = k_0 + k_Q[Q]$$

Addition of n-butyl amine (BuNH<sub>2</sub>, 5.0 mmol/L) or MeOH (50 mmol/L) to the hexane solutions of 2a had similar effects as AcOH on the overall transient behavior (Fig. 1), eliminating the absorptions owing to Ph<sub>2</sub>Ge and its products and leaving behind the same long-lived transient species that is observed in the presence of AcOH. Like the carboxylic acid, both of these reagents are potent germylene scavengers, reacting with Ph2Ge at close to the diffusioncontrolled rate in both cases (9).<sup>3</sup> Addition of carbon tetrachloride (CCl<sub>4</sub>), chloroform (CHCl<sub>3</sub>), or oxygen (O<sub>2</sub>) to hexane solutions of 2a in hexane containing 50 mmol/L MeOH caused an increase in the decay rate of the surviving longlived transient (monitored at 440 nm) in proportion to the concentration of added reagent, and plots of  $k_{decay}$  vs. [Q] according to eq. [7] were linear, with slopes of  $k_{\text{decay}}$  vs. [Q] according to eq. [7] were linear, with slopes of  $k_{\text{CC1}_4} = (7.3 \pm 0.7) \times 10^6 \text{ mol/L}^{-1} \text{ s}^{-1}$ ,  $k_{\text{CHC1}_3} = (1.2 \pm 0.1) \times 10^4 \text{ mol/L}^{-1} \text{ s}^{-1}$  and  $k_{\text{O}_2} = (6.6 \pm 0.8) \times 10^7 \text{ mol/L}^{-1} \text{ s}^{-1}$  for CCl<sub>4</sub>, CHCl<sub>3</sub>, and O<sub>2</sub>, respectively. The  $k_{\text{O}_2}$  value is in good agreement with that reported for this species in the original study  $(k_{O_2} = 1.02 \times 10^8 \text{ mol/L}^{-1} \text{ s}^{-1})$  (2). It is interesting to note that the transient exhibits similar (but two to three times greater) reactivity towards O2 and CCl4 as Ph2Ge does under similar conditions (10), but exhibits ca. 20 times lower reactivity toward CHCl<sub>3</sub> (10).

Finally, we examined the flash photolysis behavior of 2a in deoxygenated tetrahydrofuran (THF) solution, as Ph2Ge and other reactive germylenes are known to form Lewis acid-base complexes with ethers, with substantially blueshifted absorption maxima compared to those of the free species (16, 17); for example, generation of  $Ph_2Ge$  in a 2methyltetrahydrofuran glass at 77 K leads to a species absorbing at  $\lambda_{\text{max}} = 325$  nm, which was assigned to the germylene-ether complex (17). The transient spectra obtained by flash photolysis of 2a in THF solution are similar to those of Fig. 1b, but exhibit a weak shoulder on the long wavelength edge of the rising 310 nm absorption, consistent with the presence of the Ph2Ge-complex. The spectrum of the complex could be isolated by addition of 0.2 mol/L CCl<sub>4</sub> to the solution, which shortened the lifetime of the 310/445 nm transient absorptions to ca. 500 ns and left behind longer lived absorptions ( $\tau \sim 2 \ \mu s$ ), centered at  $\lambda_{max} =$ 345 nm that decayed with second-order kinetics (see Fig. 4). The spectrum is in reasonably good agreement with that assigned to the Ph<sub>2</sub>Ge–THF Lewis acid–base complex (eq. [8]) in the earlier matrix experiments (17). From the lifetime of the 310/445 nm species under these conditions, a rate constant of ca.  $1 \times 10^7$  mol/L<sup>-1</sup> s<sup>-1</sup> can be estimated for its reaction with CCl<sub>4</sub>, in good agreement with the value measured in hexane solution (vide supra). The extended lifetime of the Ph2Ge-THF complex under these conditions presumably results from the fact that it is much less reactive toward CCl<sub>4</sub> than the free germylene, whose concentration is reduced by orders of magnitude relative to that in hexane solution owing to the solvent complexation equilibrium. The "stabilizing"

<sup>3</sup>W.J. Leigh, C.R. Harrington, F. Lollmahomed, and J.J. McDonald. To be published.

**Fig. 4.** Transient absorption spectra recorded by laser flash photolysis of a deoxygenated  $1.3 \times 10^{-4}$  mol/L solution of **2a** in THF containing 0.2 mol/L CCl<sub>4</sub>, 0.6–2.1 µs ( $\bigcirc$ ) and 81–85 µs ( $\bigcirc$ ) after the (248 nm) laser pulse. The inset shows a transient decay profile recorded at 350 nm.



effect of ethers and other Lewis bases on reactive germylenes is well-recognized (25–28).

[8] 
$$Ph_2Ge + 0$$
  $\longrightarrow$   $Ph_2Ge - 0$ 

The two most reasonable candidates for the 310/445 nm species of Fig. 1b are the diphenyl(trimethylsilyl)germyl radical (10), which our steady-state results indicate is formed upon photolysis of 2a in significant yield, and the 1germahexatriene derivative 9, which would be derived from formal 1,3-trimethylsilyl migration into the ortho position of one of the phenyl groups in the excited singlet state of 2a. While we have *no* evidence for the formation of 9 from steady-state photolysis experiments, we can nevertheless not easily discount the possibility that it is formed in minor yields and escaped detection in the product studies; trapping of germenes (and silenes) of this general structure by dienes and alcohols is known to afford more than a single product (18, 23, 29). Furthermore, photorearrangements of this type are common in arylgermasilanes (6, 18, 30) and aryldisilanes (31–33) in which the reaction was initially discovered (34). Germene 9 can be expected to be a much stronger absorber than Ph<sub>2</sub>Ge, and exhibit similar reactivity to that actually observed for the 310/445 nm transient (18).

The rationale behind the latter statement is as follows. The rate constants for reaction of AcOH and MeOH with germene **8** (one of only two germenes of this type that have been studied (18)) are on the order of  $4 \times 10^5$  mol/L<sup>-1</sup> s<sup>-1</sup> or less, three orders of magnitude lower than the homologous silene derivative (16) (18). The reactivity of **9** with nucleophiles can be expected to be significantly lower than that of **8** because of the presence of the trimethylsilyl substituent at Ge, based on analogies in transient silene chemistry; trimethylsilyl substitution at silicon in silenes reduces the re-

activity of the Si=C bond by roughly a factor of 10 relative to a methyl substituent (35), which is similar to a phenyl group in its effects on Si=C reactivity (36, 37). Finally, like its silicon counterpart (16), germene 8 exhibits significantly higher reactivity toward  $O_2$  and chlorocarbons than it does toward alcohols or other nucleophiles, owing to the radicallike nature of these reactions and the radical-stabilizing effect of the cyclohexadienyl substituent attached to the germenic carbon atom (18). These considerations suggest that the reactivity of the 310/445 nm transient species of Fig. 1b is not inconsistent with what might be expected for germene 9. The only piece of data that argues *against* this assignment is the UV absorption maximum, which lies ca. 35 nm  $(1800 \text{ cm}^{-1})$  to the *blue* of that exhibited by germene **8** (18). In silenes, replacement of a methyl substituent at silicon with a trimethylsilyl group produces a ca. 4000 cm<sup>-1</sup> red shift in the UV absorption maximum (35); this fact, coupled with the facts that replacement of one of the phenyl groups in 16 with a methyl group causes a ca. 2000  $\text{cm}^{-1}$  blue shift in the absorption maximum (23) and silenes and germenes with the same substituents exhibit essentially identical UVvis absorption maxima (18, 38), leads to the expectation that the absorption maximum of 9 should be quite similar to that of 8 ( $\lambda_{max} \sim 475$  nm).



To address the other possible transient assignment, germyl radical 10, we have independently generated the radical by hydrogen abstraction from the corresponding germyl hydride (17) by *tert*-butoxyl radicals (eq. [9]), generated by 308 nm laser flash photolysis of 5-30 mmol/L solutions of 17 in ditert-butylperoxide (BOOB) - isooctane (1:4) solution, using a similar procedure to that used previously for the generation of triphenylgermyl and other Group 14 radicals (39, 40). Figure 5 shows the resulting transient absorption spectrum of the radical, a representative transient absorption profile illustrating its growth kinetics, and a plot of the pseudo-firstorder rate constant for growth of the radical absorption vs. concentration of 17, the slope of which is the absolute rate constant for hydrogen abstraction from 17 by tert-butoxyl radical. The value obtained,  $k = (2.4 \pm 0.4) \times 10^8 \text{ (mol/L)}^{-1} \text{ s}^{-1}$ . is roughly twice higher than that for the analogous reaction of triphenylgermane (Ph<sub>3</sub>GeH) (39),<sup>4</sup> which is the expected result on the basis of comparisons of the corresponding rate constants for hydrogen abstraction from tris(trimethylsilyl)germane and triethylgermane (41), and analogies taken from silicon radical chemistry (42). A possible alternate assignment of the transient product to the diphenylgermyl radical, which might be formed by trimethylsilyl transfer from 17 rather than the expected hydrogen abstraction to form 10, can be ruled out on the basis of comparisons of the spectrum to that reported for the diphenylgermyl radical ( $\lambda_{max} = 325$ , 405 nm (39b)).<sup>5</sup> The authentic spectrum of radical **10** 

<sup>&</sup>lt;sup>4</sup>We also remeasured the rate constant for H abstraction from Ph<sub>3</sub>GeH in the course of this work and obtained a value of  $k = (1.2 \pm 0.1) \times 10^8 \text{ (mol/L)}^{-1} \text{ s}^{-1}$ , in excellent agreement with the previously reported value of  $9 \times 10^7 \text{ (mol/L)}^{-1} \text{ s}^{-1}$  (39).

**Fig. 5.** (*a*) Transient absorption spectrum of the diphenyl(trimethylsilyl)germyl radical, recorded 3.7–3.9 µs after 308 nm laser photolysis of a 0.040 mol/L solution of Ph<sub>2</sub>Ge(H)SiMe<sub>3</sub> (**17**) in BOOB–isooctane (1:4, v/v); the inset shows a typical growth profile of the radical, recorded at a monitoring wavelength of 420 nm. (*b*) Plot of  $k_{\text{growth}}$  at 420 nm vs. the concentration of added **17**. The solid line represents the linear least-squares fit of the data to eq. [6].



(Fig. 5*a*) agrees reasonably well with the spectrum of the 310/445 nm transient from photolysis of **2a** (Fig. 1*b*), although the match is not precise. We did not attempt to measure rate constants for reaction of authentic **10** with  $O_2$  or with CCl<sub>4</sub> for comparison to those for the 310/445 nm transient, the latter because the germane precursor is unstable in the presence of the halocarbon and light.



Table 1 lists the UV absorption maxima and absolute rate constants for reaction of triphenylgermyl radicals (germene **8**) and the 310/445 nm transient from flash photolysis of **2a**. As mentioned previously, the reactivity of the species is sim-

ilar to that of **8** with the same reagents, significantly more so than it is to the reactivity of the triphenylgermyl radical. In fact, a significantly lower reactivity toward halocarbons and oxygen compared to triphenylgermyl is what one would expect of radical **10**, as the stabilizing effect of trimethylsilyl substitution on both germanium and (in particular) silicon centered radicals is well-known (41–43).

#### The photochemistry of 1,4-dihydro-5-methyl-1,2,3,4,9,9hexaphenyl-1,4-germanonaphthalene (11)

Compound 11 was synthesized in ca. 80% yield by cycloaddition of 4-methylbenzyne (19) to hexaphenylgermole (18; see eq. [10]) in dichloromethane at -78 °C, by an analogous procedure to that reported for the synthesis of 4 (16). The reaction mixture also contained small amounts of the 4methylbenzyne dimerization products 20 and 6-methyl-1,2,3,4-tetraphenylnaphthalene (21); small amounts of 18 are very likely present as well, although the compound could not be specifically detected in the NMR spectrum of the mixture. The amount of 21 in the sample increased slowly relative to 11 over a few hours, thus, the latter was isolated from the reaction mixture by cold (ca. -15 °C) radial chromatography, characterized on the basis of its <sup>1</sup>H and <sup>13</sup>C NMR and mass spectra (see the Experimental section), and stored in the dark at -78 °C. However, in spite of reasonable efforts, a sample of 11 containing less than ca. 5% 21 could not be obtained.



To quantify the thermal lability of **11**, a 0.055 mol/L solution of the compound was prepared in deoxygenated cyclohexane- $d_{12}$  containing 0.5 mol/L DMB and monitored over time at 23 °C by NMR spectroscopy. The mixture contained ca. 10% **21** at the beginning of the experiment, evidently formed by thermal decomposition of **11** subsequent to its initial purification. The NMR spectrum was measured at selected time intervals over the following 20 h, which revealed slow conversion of **11** to **21** and **5** (eq. [11]). A plot of  $\log[[11]/(mol/L))$  vs. time was reasonably linear ( $r^2 = 0.9886$ ; see Fig. 6) and linear least-squares analysis afforded a first-order rate constant of  $(1.6 \pm 0.1) \times 10^{-5}$  s<sup>-1</sup> for the decomposition of **11**, which yields **21** and Ph<sub>2</sub>Ge, trapped as DMB adduct **5** at 23 °C. This corresponds to a half-life of

**Table 1.** Comparison of UV–vis absorption spectra and absolute rate constants for the reaction of the 310/445 nm transient from **2a**, triphenylgermyl radicals (Ph<sub>3</sub>Ge), and germene **8** with halocarbons and O<sub>2</sub>.

	310/445 nm Transient	Ph <sub>3</sub> Ge	8
$\lambda_{max}$ (hexane solution, nm)	310, 445	328, 405 (50)	475 (18)
$k_{\rm CC1_4} \ ((\rm mol/L)^{-1} \ s^{-1})$	$7.3 \times 10^{6}$	$5.8 \times 10^8$ (3)	$2.9 \times 10^7$ (18)
$k_{\text{CHC1}_3} \; ((\text{mol/L})^{-1} \; \text{s}^{-1})$	$1.2 \times 10^4$	5.5×10 <sup>7 6</sup>	$<3 \times 10^{6}$ (18)
$k_{\rm O_2} \ (({\rm mol/L})^{-1} \ {\rm s}^{-1})$	6.6×10 <sup>7</sup>	$3.8 \times 10^9$ (3)	$9.6 \times 10^7$ (18)

ca. 12 h, or (put another way) a decomposition rate of ca. 6% per hour at 23 °C.



Steady-state photolysis of 11 was carried out on argon outgassed 0.05 mol/L solutions in cyclohexane- $d_{12}$  containing 0.5 mol/L MeOH or DMB with 254 nm light, with the course of the photolyses periodically monitored by <sup>1</sup>H NMR spectroscopy; the samples of 11 each contained ca. 10% 21 at the beginning of the experiment. While irradiations and NMR analyses were all carried out at room temperature, the samples were otherwise stored at -78 °C to minimize thermal decomposition. Irradiation to ca. 50% conversion of 11 showed 21 and the corresponding Ph<sub>2</sub>Ge trapping products (methoxygermane 13 or germacyclopentene 5) to be the only detectable photolysis products. While no attempts were made to determine the quantum yield for Ph<sub>2</sub>Ge extrusion from the compound, it was estimated to be of similar magnitude to that from 5 for which a value of  $\Phi = 0.62$  has been reported (9). Görner et al. (44) reported a quantum yield of  $\Phi = 0.4$  for the extrusion of Me<sub>2</sub>Ge from the related compound 22 in deoxygenated methylcyclohexane solution.



Laser flash photolysis experiments were carried out with flowing, argon outgassed solutions of freshly chromatographed **11** (ca.  $5 \times 10^{-5}$  mol/L, containing ca. 5% **21**) in anhydrous hexane, again using the KrF excimer laser as excitation source. Figure 7 shows a series of transient absorption spectra recorded at various time intervals over the first

<sup>6</sup>W.J. Leigh and N.P. Toltl. Unpublished results.

**Fig. 6.** The thermal decomposition of germanorbornadiene **11** in cyclohexane- $d_{12}$  at 23 °C. The solid line represents the linear least-squares fit of the data, affording a first-order rate constant  $k = (1.6 \pm 0.1) \times 10^{-5} \text{ s}^{-1}$ ,  $r^2 = 0.9886$ ).



3.6 µs after the laser pulse. The results are consistent with the formation of at least three transient species. The shortest lived transient exhibits very strong absorptions centered at  $\lambda_{max}$  = 360 nm, is formed with the laser pulse, and decays with a lifetime of  $\tau \sim 300$  ns. The second species is assigned to the weak shoulder on the 360 nm band in the 50-150 ns spectrum. Its apparent absorption maximum is ca. 480 nm (see the expanded spectra in Fig. 7b), which is clearly an underestimate caused by the substantial overlap with the 360 nm band. Nevertheless, the absorptions in the 460-540 nm region of the spectrum are at least five times more intense than would be expected if Ph2Ge was the only contributor to the absorptions in this range, assuming the germylene is produced at an initial concentration of ca. 10 µmol/L, which is the maximum value we would expect under the conditions of our experiments. The third species is significantly longer lived than the other two and exhibits an apparent  $\lambda_{max} \sim 460$  nm, too far to the red to be assigned to the expected germylene dimerization product (digermene 15). While it is perhaps relevant to point out that the spectrum of this species is similar to that reported in the previous matrix photolysis of 4 (1), we have insufficient information to make a reliable assignment of the species. At no monitoring wavelength in the range studied was a growth in the transient signal discernible, although this is to be expected

**Fig. 7.** (*a*) Transient absorption spectra recorded by laser flash photolysis of a deoxygenated  $5 \times 10^{-5}$  mol/L solution of **11** in anhydrous hexane at 23 °C, 50–150 ns ( $\bigcirc$ ) and 3.2–3.5 µs ( $\square$ ) after the (248 nm) laser pulse; the inset shows a transient decay profile recorded at 360 nm. (*b*) An expanded plot of the spectra of (*a*) with a spectrum recorded 1.4–1.6 µs after the pulse included; the vertical line marks the apparent maximum of the long wavelength absorption band in the 50–150 ns spectrum.



considering the substantial overlap with the strongly absorbing species at 360 nm.

Similar experiments carried out on an O<sub>2</sub> saturated solution of **11** verified that Ph<sub>2</sub>Ge and its oligomerization products contribute in only a very minor way, if at all, to the transient absorptions observed from flash photolysis of this compound. Under these conditions the transient at 500 nm exhibited a lifetime of ca. 75 ns, and decayed to a residual absorption level roughly 4% of that immediately present after the pulse. A quenching rate constant of  $k_{O_2} \sim 9 \times 10^8 \text{ (mol/L)}^{-1} \text{ s}^{-1}$  can be estimated from the lifetime (using a value of  $[O_2] = 0.015 \text{ mol/L}$  for the concentration of  $O_2$  in  $O_2$  saturated hexane), which is ca. 30 times higher than the rate constant reported by us recently for the reaction of Ph<sub>2</sub>Ge with O<sub>2</sub> ( $k_{O_2} \sim 2.7 \times 10^7 \text{ (mol/L)}^{-1} \text{ s}^{-1}$  (10)). The other major change noted upon saturation of the solution with O<sub>2</sub> was a change in the form of the decay of the 360 nm transient to biexponential kinetics, with roughly

65% of the absorptions decaying on a very fast timescale and the remaining ~35% exhibiting a lifetime similar to that observed in the absence of  $O_2$ . This behaviour suggests that the transient absorptions produced upon flash photolysis of **11** are dominated by triplet or triplet-derived species.

Our results for **11** are similar to those reported for the related compound **22** by Görner and co-workers (44), who assigned the transients observed upon 248 nm laser flash photolysis of the compound to the triplet state of 1,2,3,4-tetraphenylnaphthalene, the coproduct of Me<sub>2</sub>Ge photoex-trusion from this compound. They were similarly unable to obtain discrete evidence for the formation of a transient assignable to the germylene (44).

As was also reported in the earlier study of **22** (44), virtually identical transient spectroscopic behaviour was observed upon laser flash photolysis of (static)  $1 \times 10^{-5}$  mol/L solutions of the tetraphenylnaphthalene coproduct (**21**, in the present case) in both deoxygenated and oxygen saturated hexane solution, with the transient spectra and lifetimes at various wavelengths coinciding quite closely to those obtained using **11** under corresponding conditions. In this case, saturation of the solution with O<sub>2</sub> decreased the lifetime of the 500 nm transient absorptions to ca. 50 ns from which can be estimated a quenching rate constant of  $k_{O_2} \sim 1.3 \times 10^9 \text{ (mol/L)}^{-1} \text{ s}^{-1}$ , in good agreement with that obtained in experiments using **11** as the precursor.

Görner and co-workers (44) explained their results for 22, which were much more extensive than the present ones for 11 and involved purer samples (22 is evidently significantly more stable thermally than 11 (19)), in terms of a mechanism in which the (1,2,3,4-tetraphenylnaphthalene) coproduct of Me<sub>2</sub>Ge extrusion is formed in the excited singlet state, which then yields the triplet after intersystem crossing. The alternative possibility that the naphthalene triplet is directly produced along with (singlet) Me<sub>2</sub>Ge from the triplet state of the precursor was ruled out on the basis of CIDNP experiments. Because our samples of 11 contained small amounts of the corresponding naphthalene derivative (21), we cannot ascertain to what extent the transient mixture produced in our experiments with the Ph<sub>2</sub>Ge precursor is contaminated by cophotolysis of the impurity. Nevertheless, our results verify that the transient spectroscopic behaviour observed in flash photolysis experiments with compounds of this type is dominated by triplet and (or) triplet-derived species (for one reason or another), and that simple germylenes such as Ph<sub>2</sub>Ge or Me<sub>2</sub>Ge are impossible to detect reliably (if at all) in fluid solution from such precursors by time-resolved UV spectroscopic methods.

# **Summary and conclusions**

In spite of the indication from product studies that the direct photolyses of disilylgermane 2a and benzogermanorbornadiene 11 afford Ph<sub>2</sub>Ge in very high yields, they are clearly unsuitable as precursors of the germylene for study by time-resolved UV-vis spectroscopic methods in solution. In the case of 2a, this is due to the competing formation of a second transient product, which, although it is formed in relatively low yield, absorbs strongly over the same spectral range as Ph<sub>2</sub>Ge and its dimerization product (digermene 15), and is much longer lived than the relatively weakly absorbing germylene. The germylene and its dimer *can* be successfully detected in laser flash photolysis experiments with this compound, but their relatively weak absorptions are superimposed on a background of intense, relatively long-lived absorptions owing to the minor product. This makes them very easy to miss altogether, particularly when little or no independent information on their spectra and reactivities exists, as was the case in the original study. The UV-vis absorption spectrum of the species and its reactivity toward halocarbons and oxygen is broadly consistent with its assignment to the diphenyl(trimethylsilyl)germyl radical, which product studies show is formed in minor, but significant, yields upon photolysis of 2a. Radical formation is suppressed in the presence of high concentrations of diene, suggesting that the Si-Ge bond homolysis process that is responsible for its formation is derived from the triplet state of the disilylgermane. The alternate assignment of the species to germene 9 cannot be ruled out.

Other factors frustrate attempts to detect the germylene and its dimer in laser flash photolysis experiments with the benzogermanorbornadiene derivative 11, in spite of the fact that product studies indicate its photodecomposition to proceed cleanly and in relatively high quantum yield. One of these is the compound's rather low thermal stability, which makes it exceedingly difficult to purify to the level necessary for studies of this type; the major product of thermal decomposition (tetraphenylnaphthalene derivative 21) absorbs strongly at the wavelength necessary to excite the germylene precursor, and its relatively efficiently populated triplet state absorbs very strongly over the same range as the germylene does. Earlier studies with a related compound (44) indicate that even when highly pure samples of the precursor can be obtained, the only transients detectable by time-resolved UV spectroscopic methods are derived from the excited triplet state of the aromatic coproduct. This is thought to be due to the fact that the photodecomposition reaction proceeds adiabatically, ultimately yielding the coproduct in its excited triplet state. In the present experiments with 11, these two complicating factors combine to make the triplet state of tetraphenylnaphthalene 21 the dominant transient detectable upon laser flash photolysis of the compound in solution at ambient temperatures.

# **Experimental**

<sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra were recorded on Bruker AV 200 or AV 600 spectrometers in deuteriochloroform solution unless otherwise noted; <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced to the residual solvent proton and <sup>13</sup>C signals, respectively. High-resolution electron impact and atmospheric pressure chemical ionization (APCI) mass spectra and exact masses were determined on a Micromass TofSpec 2E (MALDI-TOF mass spectrometer) performed on a Micromass Ultima ESI/APCI triple quadrupole mass spectrometer. IR spectra were recorded on a BioRad FTS-40 FT IR spectrometer and are reported in wavenumbers  $(cm^{-1})$ . Gas chromatographic analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a conventional heated injector, a flame ionization detector, a Hewlett-Packard 3396A integrator, and a SPB-5 capillary column (25 m, 0.25 µm, Supelco, Inc., Bellefonte, Pennsylvania), while GC–MS analyses were carried out using a Micromass GCT instrument interfaced to an Agilent 6890 Series GC system with a J & W DB-XLB 30 m column. Melting points were determined using a Mettler FP82 hot stage mounted on a polarizing microscope and are uncorrected. Radial chromatographic separations were carried out using a Chromatotron<sup>®</sup> (Harrison Research, Inc., Palo Alto, California) with silica gel 60 plates (4 mm thick) and with hexane as the eluant. Column chromatography was performed on a 30 mm × 600 mm column using silica gel (~100 g, acid washed, 230–400 mesh) (Silicycle). Steady-state photolyses were carried out in a Rayonet<sup>®</sup> photochemical reactor (Southern New England Ultraviolet Co., Branford, Connecticut) equipped with a merry-go-round apparatus and six RPR-2537 lamps (254 nm).

4-Methyl-2-nitroaniline (Sigma-Aldrich, St. Louis, Missouri), chlorotrimethylsilane (Gelest, Morrisville, Pennsylvania), tert-butyllithium (1.7 mol/L in pentane, Sigma-Aldrich), dimethylmalonate (Sigma-Aldrich), and lead tetraacetate (Sigma-Aldrich) were used as received from the suppliers. 2,3-Dimethyl-1,3-butadiene (Sigma-Aldrich) was purified before use by bulb-to-bulb distillation under vacuum. Tetrahydrofuran and hexanes (Caledon reagent grade, Georgetown, Ontario) were dried by passage through activated alumina under nitrogen using a Solv-Tek solvent purification system (Solv-Tek, Inc., Berryville, Virginia). Dichloromethane, methanol, acetone and pentane (all Caledon reagent grade) were used as received. Triethylamine (Sigma-Aldrich) was refluxed over solid KOH and distilled before use. 1,1,2,3,4,5-Hexaphenylgermole was prepared by the procedure of Ferman et al. (45).

# Bis(trimethylsilyl)diphenylgermane (2a)

To a flame-dried 150 mL two-neck round-bottom flask equipped with a rubber septum, magnetic stirring bar, and nitrogen inlet was added anhydr. THF (30 mL) via a syringe. The solution was cooled to -40 °C (MeCN-CO<sub>2</sub> bath) and 5.2 g (22.8 mmol) of diphenylgermane was added by syringe dropwise through the septum. A solution of tert-butyllithium (1.7 mol/L in pentane, 32 mL, 54.4 mmol) was then added dropwise using a syringe in several portions over 10 min. The initial brilliant yellow reaction mixture because of the diphenylgermyl anion transformed to a dark red solution after the half-way point of the addition, signifying the presence of the diphenylgermyl dianion (Ph2GeLi2) (46). The solution was stirred at -40 °C for 25 min and then neat chlorotrimethylsilane (9 mL, 7.7 g, 71.3 mmol) was added dropwise via a syringe, causing a slight increase in temperature and the mixture to turn yellow and cloudy. The cooling bath was removed and the reaction mixture was stirred for 24 h, during which time a white precipitate formed. Saturated aqueous ammonium chloride was added slowly until the precipitate dissolved, diethyl ether (25 mL) was added, the layers were separated, and the aqueous portion was extracted with additional ether  $(3 \times 25 \text{ mL})$ . The combined ether extracts were washed with saturated brine (25 mL) and water (25 mL), dried over anhydrous magnesium sulphate, filtered, and the solvent was removed on the rotary evaporator. The resulting yellow oil was purified by vacuum distillation (6.7 g, 18.1 mmol, 79%, 110 °C (0.02 mmHg, 1 mmHg = 133.322 4 Pa)) and recrystallized at -40 °C several times from acetone–methanol (1:1, *v/v*) to yield colourless needles with a melting point of approximately –20 °C. The compound was identified as **2a** by comparison of its <sup>1</sup>H and <sup>13</sup>C NMR and mass spectra to the previously reported data (6). The purity was estimated to be >99.5% by GC. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 0.20 (s, 18H), 7.21–7.24 (m, 6H), 7.34–7.39 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 0.33, 127.5, 128.1, 135.8, 139.4. MS (EI) *m/z*: 376 (1, <sup>76</sup>Ge), 374 (5, <sup>74</sup>Ge), 372 (3, <sup>72</sup>Ge), 370 (2, <sup>70</sup>Ge), 359 (20), 357 (15), 355 (10), 301 (10), 299 (7), 297 (5), 226 (36), 224 (75), 222 (68), 220 (65), 197 (67), 151 (40), 149 (32), 147 (27), 136 (33), 135 (100), 107 (23), 73 (65), 45 (25). Exact mass calcd. for C<sub>18</sub>H<sub>28</sub>GeSi<sub>2</sub>: 374.0941; found: 374.0950.

# 1,1,2,2-Tetraphenyl-1,2-bis(trimethylsilyl)digermane (14)

To a flame-dried 25 mL one-neck round-bottom flask equipped with a septum and magnetic stirring bar, under nitrogen, was added 1,1,2,2-tetraphenyldigermane (0.51 g, 1.12 mmol) (47) in anhydr. THF (4 mL) via a syringe. The solution was cooled to -40 °C (MeCN-CO<sub>2</sub> bath) and tertbutyllithium (1.4 mL, 2.38 mmol) was added dropwise via a syringe in several portions over 10 min. The dark yellow reaction mixture was stirred for 40 min at -40 °C and chlorotrimethylsilane (0.4 mL, 3 mmol) was added dropwise via a syringe over 2 min, causing the mixture to turn colourless. The reaction mixture was warmed to ambient temperature and stirred for 1 h after which saturated aqueous ammonium chloride (2 mL) and distilled water (4 mL) were added slowly until the solution clarified. The work up consisted of dilution with diethyl ether (20 mL) and extraction of the aqueous layer with more ether  $(2 \times 20 \text{ mL})$ . The combined organic layers were washed with saturated brine (20 mL) and distilled water (20 mL), dried over magnesium sulphate, filtered, and the solvent was removed on the rotary evaporator. The resulting colourless solid (>95% pure by NMR) was identified as 14 (mp 212-214 °C) on the basis of the following spectroscopic data: IR (solid): 3066 (s), 2956 (m), 1580 (w), 1481 (m), 1429 (m), 1245 (s), 1046 (s), 833 (s). <sup>1</sup>H NMR ( $C_6D_6$ )  $\delta$ : 0.14 (s, 18H), 7.11 (t, J = 7.2 Hz, 4H), 7.15 (t, J = 7.2 Hz, 8H) 7.64 (d, J = 7.8 Hz, 8H). <sup>13</sup>C NMR ( $C_6D_6$ )  $\delta$ : 0.24, 128.3, 128.4, 136.5, 139.8. <sup>29</sup>Si NMR  $(C_6D_6) \delta$ : -6.1. MS (EI) *m*/*z*: 602 (1), 601 (1), 600 (2), 599 (1), 598 (1.5), 587 (4), 585 (5), 583 (4), 529 (4), 527 (5), 525 (4), 451 (60), 450 (98), 448 (100), 446 (50), 301 (69), 299 (55), 297 (43), 151 (56), 149 (45), 147 (34). Exact mass calcd. for C<sub>30</sub>H<sub>38</sub>Ge<sub>2</sub>Si<sub>2</sub>: 602.0936; found: 602.0947.

#### **Diphenyltrimethylsilylgermane** (17)

To a 50 mL Schlenk tube connected to a vacuum line and equipped with a magnetic stirring bar was added diphenylgermane (1.18 g, 5.16 mmol) and freshly distilled THF (5 mL). The tube was cooled to -40 °C and *tert*-butyllithium in hexane (1.58 mol/L, 3.26 mL, 5.16 mmol)) was added over 5 min. The resulting yellow mixture was allowed to warm to -20 °C and then stirred for 20 min after which chlorotrimethylsilane (1 mL, freshly distilled from calcium hydride) was added via a syringe, causing the immediate formation of a colourless precipitate. The mixture was warmed to room temperature and stirred for 1 h after which the solvent and excess chlorosilane were removed under high vacuum. The residue was extracted with dry pentane; removal of the pentane under vacuum afforded a colourless liquid. The product was further purified by bulb-to-bulb distillation (twice) to yield a colourless solid (0.55 g, 1.83 mmol, 35%, mp 36.0–37.2 °C), which was identified as **17** on the basis of the following spectral data: IR (solid): 3068 (m), 2955 (s), 2915 (s), 1998 (s, Ge-H), 1483 (m), 1430 (m), 1246 (s), 1088 (m), 976 (w), 836 (s). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 0.18 (s, 9H), 5.08 (s, 1H), 7.12–7.18 (m, 6H), 7.55–7.57 (m, 4H). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$ : –0.63, 128.5, 128.6, 135.8, 137.4. <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$ : –10.1. MS (EI) *m/z*: 299.7 (2), 229.9 (13), 228.9 (31), 227.9 (86), 227.0 (100), 226.0 (86), 225.0 (70), 224.1 (56), 223.1 (44), 198.1 (6), 197.1 (25), 195.2 (6), 154.1 (5) 153.1 (15), 152.1 (14), 151.1 (58), 150.1 (15), 149.1 (45), 148.1 (4), 147.1 (32), 136.2 (8), 135.2 (50).

1-Amino-5-methylbenzotriazole was prepared by a modification of the procedure of Campbell and Rees (48), starting from 4-methyl-2-nitronaniline and dimethyl malonate. The original synthetic work did not include NMR or MS data for the compound or its synthetic precursors, so these are listed in the following.

#### Dimethyl mesoxalate 4-methyl-2-nitrophenylhydrazone

Bronze-coloured crystals, mp 158–160 °C. IR (neat): 2991 (m), 1745 (s), 1725 (s), 1450 (w), 1368 (m), 1174 (m), 944 (w). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.35 (s, 3H), 3.87 (s, 3H), 3.93 (s, 3H), 7.24 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.5 Hz, 1H), 7.97 (s, 1H), 14.08 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 20.3, 52.5, 52.6, 117.1, 124.1, 127.2, 133.4, 134.4, 136.2, 136.9, 161.8, 163.2. MS (EI) *m*/*z*: 295 (2), 141 (5), 89 (6), 87 (20), 72 (100), 71 (99), 57 (85). Exact mass calcd. for C<sub>12</sub>H<sub>13</sub>N<sub>3</sub>O<sub>6</sub>: 295.0804; found: 295.0802.

#### Dimethyl mesoxalate 2-amino-4-methylphenylhydrazone

Orange granules, mp 128 to 129 °C. IR (neat): 3464 (m), 3311 (w), 2990 (w), 1745 (s), 1725 (s), 1680 (m), 1651 (m), 1530 (s), 1440 (m), 1360 (s), 1240 (s), 1200 (m), 800 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.22 (s, 3H), 3.80 (s, 3H), 3.86 (s, 3H), 5.0 (bs, 2H), 6.52 (d, J = 8.4 Hz, 1H), 6.54 (s, 1H), 6.90 (d, J = 8.4 Hz, 1H), 13.29 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 20.9, 51.8, 51.9, 112.8, 118.5, 119.0, 119.2, 124.4, 136.1, 137.0, 163.4, 164.4. MS (EI) *m*/*z* 265 (2), 263 (3), 205 (8), 177 (5), 159 (5), 146 (5), 133 (5), 120 (10), 119 (12), 91 (50), 85 (80), 84 (100), 71 (60), 49 (85). Exact mass calcd. for C<sub>12</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>: 265.1063; found: 265.1067.

#### Dimethyl (5-methylbenzotriazol-1-yl)iminomalonate

Yellow powder, mp 115 to 116 °C. IR (neat): 2990 (w), 1745 (s), 1625 (m), 1430 (w), 1300 (m), 1240 (s), 1160 (m), 1030 (s), 812 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.51 (s, 3H), 3.99 (s, 3H), 4.02 (s, 3H), 5.1 (bs, 2H), 7.44 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.79 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 21.4, 53.5, 53.8, 110.2, 119.4, 130.2, 132.0, 136.2, 140.0, 145.3, 160.8, 162.5. MS (EI) *m*/*z*: 276 (2), 205 (4), 177 (6), 120 (5), 119 (7), 91 (15), 88 (28), 86 (95), 84 (100), 51 (70), 49 (99), 47 (55). Exact mass calcd. for C<sub>12</sub>H<sub>12</sub>N<sub>4</sub>O<sub>4</sub>: 276.0859; found: 276.0864.

#### 1-Amino-5-methylbenzotriazole

Colourless needles, mp 91 to 92 °C (lit. value (48) mp 87 to 88 °C). IR (neat): 3295 (m), 3180 (m), 2990 (w), 1745

(m), 1725 (m), 1235 (m), 1150 (m), 1110 (m), 958 (s), 810 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.46 (s, 3H), 5.73 (s, 2H), 7.28 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.66 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 21.4, 109.3, 118.4, 129.9, 130.9, 134.1, 145.0. MS (EI) *m*/*z*: 148 (4), 133 (4), 120 (25), 119 (35), 92 (20), 91 (90), 86 (75), 84 (100), 77 (15), 65 (22), 51 (17), 50 (75). Exact mass calcd. for C<sub>7</sub>H<sub>8</sub>N<sub>4</sub>: 148.0749; found: 148.0750.

# 1,4-Dihydro-5-methyl-1,2,3,4,9,9-hexaphenyl-1,4-germanonaphthalene (11)

1,4-Dihydro-5-methyl-1,2,3,4,9,9-hexaphenyl-1,4-germanonaphthalene (11) was prepared using the method of Ando et al. (17) for the synthesis of 4. To a flame-dried 100 mL twoneck round-bottom flask equipped with an addition funnel and magnetic stir bar under N2 was added anhydrous dichloromethane (30 mL) containing 1,1,2,3,4,5-hexaphenylgermole (2.00 g, 3.42 mmol) and 1-amino-5-methylbenzotriazole (0.53 g, 3.59 mmol). The resulting yellowish solution was cooled to -78 °C (*i*-PrOH-CO<sub>2</sub> bath) and a solution of lead tetraacetate (1.67 g, 3.77 mmol) in anhydrous dichloromethane (15 mL) added dropwise with stirring over 50 min. The resulting brown-tinged solution was allowed to warm gradually to room temperature over 1.5 h and then quenched with saturated aqueous sodium carbonate (20 mL). The organic layer was separated, dried with magnesium sulfate, filtered, and the solvent was removed on the rotary evaporator to yield a yellow oil. The oil was purified by radial chromatography in the freezer at -15 °C using precooled dichloromethane-pentane (1:3, v/v) as the eluant, which yielded three easily separable fractions. The first two fractions were identified as a 1:1 mixture of 3(3')-dimethylbiphenylene and 3(4')-dimethylbiphenylene (**20a** and **20b**, respectively, 0.05 g, 0.28 mmol) (49) and 6-methyl-1,2,3,4tetraphenylnaphthalene (21) (0.35 g, 0.78 mmol) by comparison of their <sup>1</sup>H NMR spectra to the literature data. The third fraction (1.8 g, 2.67 mmol, 78%) consisted of a pale yellow powder that was identified as 11 on the basis of the following spectroscopic data: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.34 (s, 3H), 6.62 (bs, 4H), 6.80 (d, J = 7.2 Hz, 2H), 6.90–6.96 (m, 7H), 7.07–7.13 (m, 12H), 7.19 (d, J = 7.2 Hz, 1H), 7.39 (d, J =7.2 Hz, 2H), 7.39 (t, J = 7.2 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H), 7.75 (d, J = 7.2 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 21.5, 61.1, 64.4, 121.8, 122.9, 124.9, 125.5, 125.7, 127.1, 127.6, 128.0, 128.3, 129.7, 129.9, 130.0, 130.1, 131.5, 133.7, 135.0, 135.8, 136.1, 137.1, 138.0, 138.1, 138.3, 138.4, 145.1, 145.8, 146.2, 147.9. MS (APCI) *m*/*z*: 677.2 (20, <sup>76</sup>Ge, M + 1), 675.2  $(100, {}^{74}\text{Ge}, M + 1), 673.1 (60, {}^{72}\text{Ge}, M + 1), 671.2 (45, )$  $^{70}$ Ge, M + 1).

# Steady-state photolysis experiments

Steady-state photolysis of a deoxygenated solution (ca. 0.75 mL) of **2a** (0.05 mol/L) in cyclohexane- $d_{12}$  containing DMB (0.1 mol/L) was carried out in a quartz NMR tube, monitoring the reaction periodically by <sup>1</sup>H NMR spectroscopy over the 0%–16% conversion range. The NMR spectra of the photolysate showed the growth of peaks assignable to hexamethyldisilane (Si<sub>2</sub>Me<sub>6</sub>,  $\delta$  0.049) and **5** ( $\delta$ : 1.78 (s, 6H) 1.97 (s, 4H), 7.20–7.24 (m, 6H), 7.40–7.43 (m, 4H)) on the basis of comparisons with the spectra of authentic samples; the relative intensities of the Si<sub>2</sub>Me<sub>6</sub> singlet and the  $\delta$  1.78 ppm singlet owing to **5** averaged to 1.0:3.24, indicating

a relative yield of 1:1.08. No other peaks were evident in the 0-0.3 ppm region of the spectrum, although it should be noted that the signal owing to PhSiMe<sub>3</sub> ( $\delta$  0.233) is almost coincident with that owing to 2a ( $\delta$  0.228). In a second experiment, a deoxygenated hexane solution containing 2a (0.01 mol/L) and DMB (0.03 mol/L) was photolyzed to ca. 60% conversion with periodic monitoring by GC. The product mixture contained (in order of increasing elution time) PhSiMe<sub>3</sub> (2.3%), **12** (2.5%), **5** (41%), and **2a** (50%); Si<sub>2</sub>Me<sub>6</sub> elutes with the solvent under these conditions. The products were identified by GC-MS analysis; the product assigned to 12 exhibited the following mass spectrum: MS (EI) m/z: 308  $(2, {}^{76}\text{Ge}), 306 (8, {}^{74}\text{Ge}), 304 (5, {}^{72}\text{Ge}), 302 (3, {}^{70}\text{Ge}), 291$ (2), 289 (1), 287 (1), 226 (6), 224 (42), 222 (28), 220 (19), 156 (39), 154 (25), 152 (17), 151 (17), 149 (12), 147 (10), 136 (19), 135 (100), 73 (40), 45 (5).

Steady-state photolysis of a deoxygenated solution (ca. 0.75 mL) of **2a** (0.05 mol/L) in cyclohexane- $d_{12}$  containing MeOH (0.5 mol/L) was carried out in a similar manner to that previously described for the DMB trapping experiment. The NMR spectra of the photolysate showed the growth of peaks assignable to  $Si_2Me_6$  ( $\delta$  0.049), **13** ( $\delta$ : 3.54 (s, 3H), 6.12 (s, 1H), 7.2-7.32 (m, 6H), 7.51-7.53 (m, 4H)), and 14 (δ: 0.027 (s, 18H), 7.15–7.19 (m, 12H), 7.36–7.40 (m, 8H)) on the basis of comparisons with the spectra of authentic samples, together with two additional Me<sub>3</sub>Si containing species ( $\delta$  0.057 and 0.063), which were not identified; the relative intensities of the Si<sub>2</sub>Me<sub>6</sub> singlet, the MeO singlet owing to 13 ( $\delta$  3.54), and the –SiMe<sub>3</sub> singlets owing to 14 ( $\delta$  0.027) and the two unidentified components were  $1.00: 0.139 \pm$  $0.013 : 0.114 \pm 0.020 : 0.103 \pm 0.027 : 0.121 \pm 0.006$ . This gives average relative yields of  $1.0: 0.84 \pm 0.07: 0.11 \pm$  $0.02: 0.20 \pm 0.05: 0.24 \pm 0.02$  for the five products, assuming that the singlets for the two unidentified components represent a single trimethylsilyl group each.

Steady-state photolyses (254 nm) of **11** were carried out in similar fashion, on argon outgassed 0.046 mol/L solutions of the compound in cyclohexane- $d_{12}$  containing methanol (0.5 mol/L) and DMB (0.5 mol/L). The photolyses were taken to ca. 60% conversion and were monitored periodically by <sup>1</sup>H NMR spectroscopy. In both cases, the formation of the diphenylgermylene adduct (**5** and **13**, respectively) was accompanied by an equal yield of **21**; no other products could be detected in yields greater than ca. 3%. The identities of the products were verified by comparison of the spectra of the crude photolysis mixtures with those of authentic samples.

#### Thermolysis of benzogermanorbornadiene 11

The thermolysis of **11** was carried out with argon outgassed 0.046 mol/L solutions of the compound in cyclohexane $d_{12}$  containing DMB (0.5 mol/L). Thermal decomposition of **11** was monitored by 200 MHz <sup>1</sup>H NMR spectroscopy, measuring the relative intensities of the  $\delta$  2.28 singlet owing to **11** and the residual proton peak owing to the solvent, every 20 min over a 24 h period. The loss of **11** was accompanied by the formation of **21** ( $\delta_{CH_2}$  2.31) and **5**.

#### Laser flash photolysis experiments

Laser flash photolysis experiments with **2a**, **11**, and **21** employed the pulses from a Lambda Physik Compex 120

excimer laser filled with F<sub>2</sub>-Kr-Ne mixtures (248 nm, ~25 ns, 100  $\pm$  5 mJ) and a Luzchem Research mLFP-111 laser flash photolysis system, modified as previously described (9). Solutions were prepared at concentrations such that the absorbance at the excitation wavelength was between ca. 0.7 and 0.9, and were continuously flowed through a vacuum oven-dried, thermostatted 7 mm  $\times$  7 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 directly inserted 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 owing to screening effects or the formation of potentially reactive species from cophotolysis of the scavenger. For experiments using oxygen as a scavenger, solutions of selected O<sub>2</sub>-N<sub>2</sub> 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.

Flash photolysis experiments with compound 17 and triphenylgermane were carried out using Professor J.C. Scaiano's system at the University of Ottawa and a Lumonics EX-530 excimer laser filled with Xe-HCl-Ne mixtures (308 nm, ~6 ns, 70  $\pm$  5 mJ) for excitation. Signals from the monochromator/photomultiplier were captured by а Tektronix 2440 digitizer and transferred to a PowerMacintosh computer programmed in the LabVIEW 4.1 environment from National Instruments (Austin, Texas). Detailed descriptions of similar laser systems have been provided elsewhere (51). Argon outgassed solutions of 18 (5-30 mmol/L) in BOOB-isooctane (1:4, v/v) were contained in 7 mm × 7 mm (static) quartz cells. Experiments were carried out at room temperature (22 °C). Growth rate constants for radical absorptions were determined by biexponential nonlinear leastsquares analysis of the growth-decay profiles, recorded at 420 nm in the case of 17 and 340 nm in the case of triphenylgermane.

Transient decay and growth rate constants were calculated by nonlinear least-squares analysis of the absorbance–time profiles using the PRISM 3.0 software package (GraphPad Software, Inc., San Diego, California) and the appropriate user-defined fitting equations, after importing the raw data from the Luzchem mLFP software. Rate constants were calculated by linear least-squares analysis of decay rate – concentration data (generally four to seven points) that spanned as large a range in transient decay rate as possible. Errors are quoted as twice the standard deviation obtained from the least-squares analyses.

# Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support, Teck Cominco Metals Ltd. for a generous gift of germanium tetrachloride, the McMaster Regional Centre for Mass Spectrometry for mass spectra, J.C. Scaiano for the use of his laser photolysis system, and M. Chretien for technical assistance. PPG and DZ are grateful for financial support from the United States National Science Foundation under grants CHE-9981715 and CHE-0316124. BKC thanks the Reactive Intermediate Student Exchange (RISE) and NSERC for summer scholarships.

#### References

- 1. W. Ando, T. Tsumuraya, and A. Sekiguchi. Chem. Lett. 317 (1987).
- S. Konieczny, S.J. Jacobs, J.K. Braddock Wilking, and P.P. Gaspar. J. Organomet. Chem. 341, C17 (1988).
- 3. K. Mochida, M. Wakasa, Y. Nakadaira, Y. Sakaguchi, and H. Hayashi. Organometallics, **7**, 1869 (1988).
- 4. M. Wakasa, I. Yoneda, and K. Mochida. J. Organomet. Chem. **366**, C1 (1989).
- 5. K. Mochida, I. Yoneda, and M. Wakasa. J. Organomet. Chem. **399**, 53 (1990).
- K.L. Bobbitt, V.M. Maloney, and P.P. Gaspar. Organometallics, 10, 2772 (1991).
- 7. N.P. Toltl, W.J. Leigh, G.M. Kollegger, W.G. Stibbs, and K.M. Baines. Organometallics, **15**, 3732 (1996).
- K. Mochida, M. Wakasa, and H. Hayashi. Phosphorus Sulfur Silicon Relat. Elem. 150–151, 237 (1999).
- 9. W.J. Leigh, C.R. Harrington, and I. Vargas-Baca. J. Am. Chem. Soc. **126**, 16105 (2004).
- W.J. Leigh and C.R. Harrington. J. Am. Chem. Soc. 127, 5084 (2005).
- K. Mochida, N. Kanno, R. Kato, M. Kotani, S. Yamauchi, M. Wakasa, and H. Hayashi. J. Organomet. Chem. 415, 191 (1991).
- 12. K. Mochida and S. Tokura. Organometallics, 11, 2752 (1992).
- K. Mochida and S. Tokura. Bull. Chem. Soc. Jpn. 65, 1642 (1992).
- K. Mochida, K. Kimijima, and H. Chiba. Organometallics, 13, 404 (1994).
- M.B. Taraban, O.S. Volkova, V.F. Plyusnin, Y.V. Ivanov, T.V. Leshina, M.P. Egorov, O.M. Nefedov, T. Kayamori, and K. Mochida. J. Organomet. Chem. 601, 324 (2000).
- W. Ando, H. Itoh, T. Tsumuraya, and H. Yoshida. Organometallics, 7, 1880 (1988).
- 17. W. Ando, H. Itoh, and T. Tsumuraya. Organometallics, **8**, 2759 (1989).
- W.J. Leigh, N.P. Toltl, P. Apodeca, M. Castruita, and K.H. Pannell. Organometallics, 19, 3232 (2000).
- 19. W.P. Neumann and M. Schriewer. Tetrahedron Lett. **21**, 3273 (1980).
- 20. J. Kocher, M. Lehnig, and W.P. Neumann. Organometallics, 7, 1201 (1988).
- 21. W.P. Neumann, E. Michels, and J. Kocher. Tetrahedron Lett. 28, 3783 (1987).
- 22. W. Ando and T. Tsumuraya. Organometallics, 8, 1467 (1989).
- 23. W.J. Leigh and G.W. Sluggett. J. Am. Chem. Soc. **115**, 7531 (1993).
- 24. W.J. Leigh and G.W. Sluggett. Organometallics, 13, 269 (1994).
- 25. P. Riviere, J. Satge, and A. Castel. C.R. Acad. Sci. Paris, **281**, 835 (1975).
- J. Barrau, M. Bouchaut, H. Lavayssiere, G. Dousse, and J. Satge. J. Organomet. Chem. 243, 281 (1983).
- 27. S. Mazieres, H. Gornitzka, and C. Couret. Polyhedron, 21, 2827 (2002).

- N.N. Zemlyansky, I.V. Borisova, M.G. Kuznetsova, V.N. Khrustalev, Y.A. Ustynyuk, M.S. Nechaev, V.V. Lunin, J. Barrau, and G. Rima. Organometallics, 22, 1675 (2003).
- 29. W.J. Leigh and G.W. Sluggett. J. Am. Chem. Soc. **116**, 10468 (1994).
- 30. K. Mochida, H. Kikkawa, and Y. Nakadaira. J. Organomet. Chem. **412**, 9 (1991).
- 31. M. Ishikawa and M. Kumada. Adv. Organomet. Chem. 19, 51 (1981).
- M. Kira and T. Miyazawa. *In* The chemistry of organic silicon compounds. *Edited by* Z. Rappoport and Y. Apeloig. John Wiley and Sons, New York. 1998. p. 1311.
- 33. M.G. Steinmetz. Chem. Rev. 95, 1527 (1995).
- M. Ishikawa, T. Fuchikami, T. Sugaya, and M. Kumada. J. Am. Chem. Soc. 97, 5923 (1975).
- W.J. Leigh, R. Boukherroub, and C. Kerst. J. Am. Chem. Soc. 120, 9504 (1998).
- T.L. Morkin, T.R. Owens, and W.J. Leigh. *In* The chemistry of organic silicon compounds. Vol. 3. *Edited by* Z. Rappoport and Y. Apeloig. John Wiley and Sons, New York. 2001. p. 949.
- 37. T.L. Morkin and W.J. Leigh. Acc. Chem. Res. 34, 129 (2001).
- 38. N.P. Toltl and W.J. Leigh. J. Am. Chem. Soc. 120, 1172 (1998).
- (a) C. Chatgilialoglu, K.U. Ingold, J. Lusztyk, A.S. Nazran, and J.C. Scaiano. Organometallics 2, 1332 (1983); (b) K.B. Clark and D. Griller. Organometallics, 10, 746 (1991).

- K.U. Ingold, J. Lusztyk, and J.C. Scaiano. J. Am. Chem. Soc. 106, 343 (1984).
- C. Chatgilialoglu and M. Ballestri. Organometallics, 14, 5017 (1995).
- 42. C. Chatgilialoglu. Chem. Rev. 95, 1229 (1995).
- S. Bernadoni, M. Lucarini, G.F. Pedulli, L. Valgimigli, V. Gevorgyan, and C. Chatgilialoglu. J. Org. Chem. 62, 8009 (1997).
- H. Görner, M. Lehnig, and M. Weisbeck. J. Photochem. Photobiol. A, 94, 157 (1996).
- 45. J. Ferman, J.P. Kakareka, W.T. Klooster, J.L. Mullin, J. Quattrucci, J.S. Ricci, H.J. Tracy, W.J. Vining, and S. Wallace. Inorg. Chem. 38, 2464 (1999).
- A. Castel, P. Riviere, J. Satge, and H.Y. Ko. Organometallics, 9, 205 (1990).
- A. Castel, P. Riviere, J. Satge, D. Desor, M. Ahbala, and C. Abdenadher. Inorg. Chim. Acta, 212, 51 (1993).
- 48. C.D. Campbell and C.W. Rees. J. Chem. Soc. (C), 742 (1969).
- 49 T. Kitamura, M. Yamane, K. Inoue, M. Todaka, N. Fukatsu, Z. Meng, and Y. Fujiwara. J. Am. Chem. Soc. **121**, 11674 (1999).
- C. Chatgilialoglu. *In* CRC handbook of photochemistry. Vol II. *Edited by* J.C. Scaiano. CRC Press, Boca Raton, Florida. 1989. p. 3.
- J.C. Scaiano, M. Tanner, and D. Weir. J. Am. Chem. Soc. 107, 4396 (1985).