

Supporting Information

Time-resolved Spectroscopic Studies of the Reactivities of Dimethylgermylene and Tetramethyldigermene in Solution.

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Figure S1. Quantum yield determination for the extrusion of GeMe₂ (trapped as **5b**) from photolysis of **3a** (0.041 M) in cyclohexane-*d*₁₂ containing 0.24 M MeOH, using the formation of methoxymethyldiphenylsilane (Ph₂MeSiOMe) from photolysis of 1,1-diphenylsilacyclobutane (Ph₂SCB; 0.037 M) in cyclohexane-*d*₁₂ containing MeOH (0.24 M) as actinometer ($\Phi_{\text{Ph}_2\text{MeSiOMe}} = 0.21 \pm 0.02$).¹ Hexamethyldisilane was used as internal integration standard. 3

Figure S2. Determination of the molar extinction coefficient of GeMe₂ at 470 nm, using the benzophenone triplet at 525 nm in dry, deoxygenated hexane ($\epsilon_{525} = 6250 \pm 1250$) as actinometer. (a) Plots of $\Delta A_{\text{max},\lambda}$ vs. laser dose for optically matched deoxygenated solutions of benzophenone and **3a** in dry hexane, excited at 248 nm; (b) expanded view of plot (a). 3

Figure S3. Transient absorption spectra from laser flash photolysis of **3b** (70 μM) in deoxygenated hexane solution at 25 °C, recorded 19-45 ns (\square), 390-415 ns (\circ), 1.48-1.50 μs (Δ), and 3.40-3.42 μs (\diamond) after the laser pulse. The inset shows typical transient growth/decay profiles, recorded at 470 nm (—) and 370 nm (\circ). The solid curve drawn through the 470 nm decay represents the best fit of the data to equation 4 ($k/\epsilon_{470} = (3.8 \pm 0.6) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$). 4

Figure S4. 600 MHz ¹H NMR spectra of the crude reaction mixture from photolysis of **3a** (0.041 M) in cyclohexane-*d*₁₂ containing MeOH (0.24 M), before (top) and after (bottom) photolysis to ca. 20% conversion. The insets in the latter spectrum are expansions showing the splitting of the signals at 0.38 and 5.28 ppm due to the product, Me₂Ge(H)OMe (**5b**). 4

Figure S5. ¹H NMR spectra of the crude reaction mixture from photolysis of **3a** (0.05 M) in cyclohexane-*d*₁₂ containing AcOH (0.25 M), before (top; 200 MHz) and after (bottom; 600 MHz) photolysis to ca. 60% conversion. The insets in the latter spectrum are expansions showing the splitting of the signals at 0.57 and 5.62 ppm due to the product, Me₂Ge(H)OAc (**5a**). 5

Figure S6. 600 MHz ¹H NMR spectra of the crude reaction mixture from photolysis of **3b** (0.051 M) in cyclohexane-*d*₁₂ containing AcOH (0.26 M) and hexamethyldisilane (0.02 M), before (top) and after (bottom) photolysis to ca. 30% conversion. 5

Figure S7. Representative decay/growth profiles for (a) GeMe₂ (monitored at 480 nm) and (b) Ge₂Me₄ (**2c**; monitored at 370 nm) as a function of Et₃GeH concentration. Figure (c) shows plots of k_{decay} and $([\Delta A_{370,\text{max}}]_0/[\Delta A_{370,\text{max}}]_Q)$ vs. [Et₃GeH] detailing the effect of the scavenger on the decay rate constant of GeMe₂ and the yield of digermene **2c**, while figure (d) shows a plot of k_{decay} for **2c** vs. [Et₃GeH].

Figure S8. Representative decay/growth profiles for (a) GeMe₂ (monitored at 480 nm) and (b) Ge₂Me₄ (**2c**; monitored at 370 nm) as a function of 2,3-dimethyl-1,3-butadiene (DMB) concentration. Figure (c) shows plots of k_{decay} and $([\Delta A_{370,\text{max}}]_0/[\Delta A_{370,\text{max}}]_Q)$ vs. [DMB] detailing the effect of the scavenger on the decay rate constant of GeMe₂ and the yield of digermene **2c**. Addition of the diene had no discernible effect on the decay time of the signal due to **2c** over the 0-0.9 mM concentration range.

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Figure S1. Quantum yield determination for the extrusion of GeMe_2 (trapped as **5b**) from photolysis of **3a** (0.041 M) in cyclohexane- d_{12} containing 0.24 M MeOH, using the formation of methoxymethyldiphenylsilane ($\text{Ph}_2\text{MeSiOMe}$) from photolysis of 1,1-diphenylsilacyclobutane (Ph_2SCB ; 0.037 M) in cyclohexane- d_{12} containing MeOH (0.24 M) as actinometer ($\Phi_{\text{Ph}_2\text{MeSiOMe}} = 0.21 \pm 0.02$).¹ Hexamethyldisilane was used as internal integration standard.

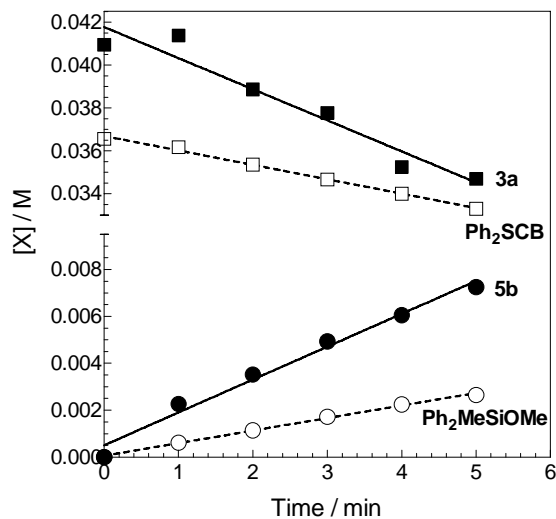


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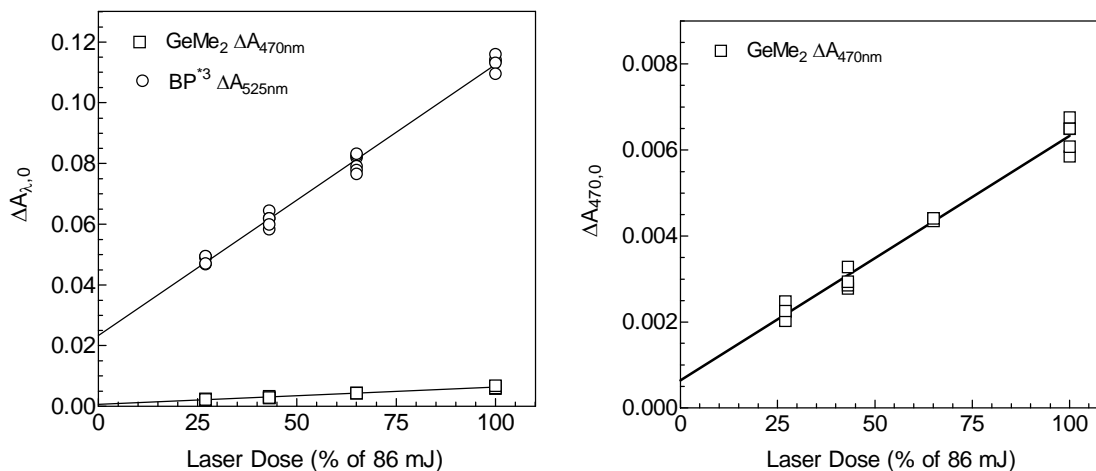


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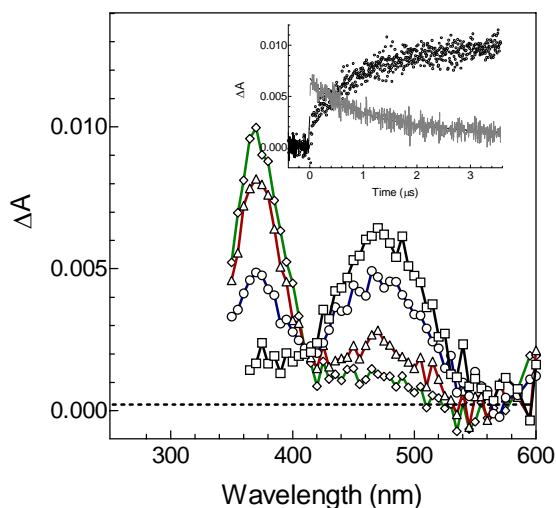


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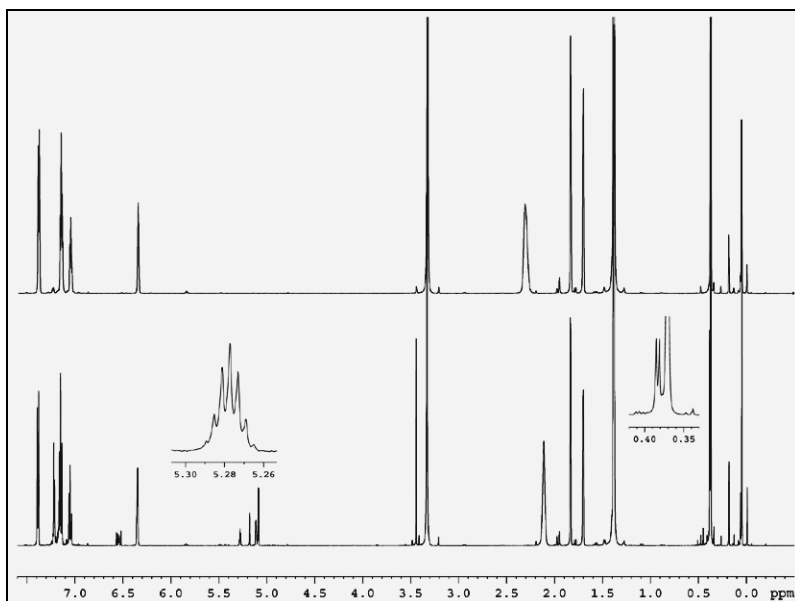


Figure S5. ^1H NMR spectra of the crude reaction mixture from photolysis of **3a** (0.05 M) in cyclohexane- d_{12} containing AcOH (0.25 M), before (top; 200 MHz) and after (bottom; 600 MHz) photolysis to ca. 60% conversion. The insets in the latter spectrum are expansions showing the splitting of the signals at 5.62 and 0.57 ppm due to the product, $\text{Me}_2\text{Ge}(\text{H})\text{OAc}$ (**5a**).

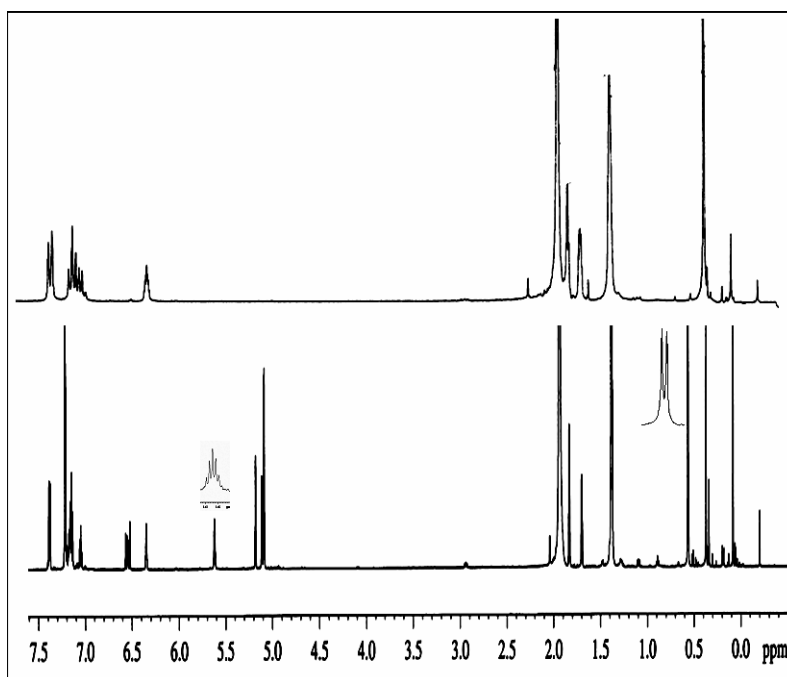


Figure S6. 600 MHz ^1H NMR spectra of the crude reaction mixture from photolysis of **3b** (0.051 M) in cyclohexane- d_{12} containing AcOH (0.26 M) and hexamethyldisilane (0.02 M), before (top) and after (bottom) photolysis to ca. 30% conversion. The insets in the latter spectrum are expansions showing the splitting of the signals at 5.62 and 0.57 ppm due to the product, $\text{Me}_2\text{Ge}(\text{H})\text{OAc}$ (**5a**).

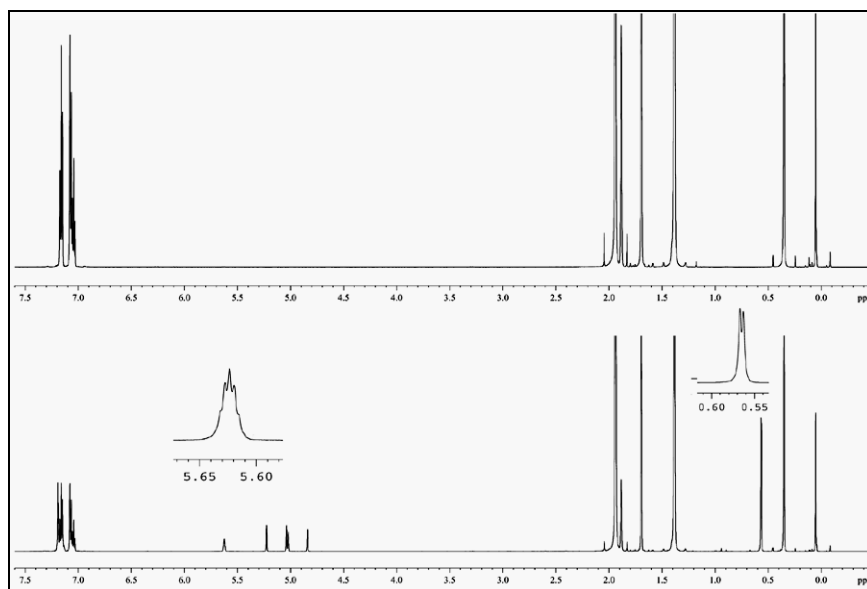


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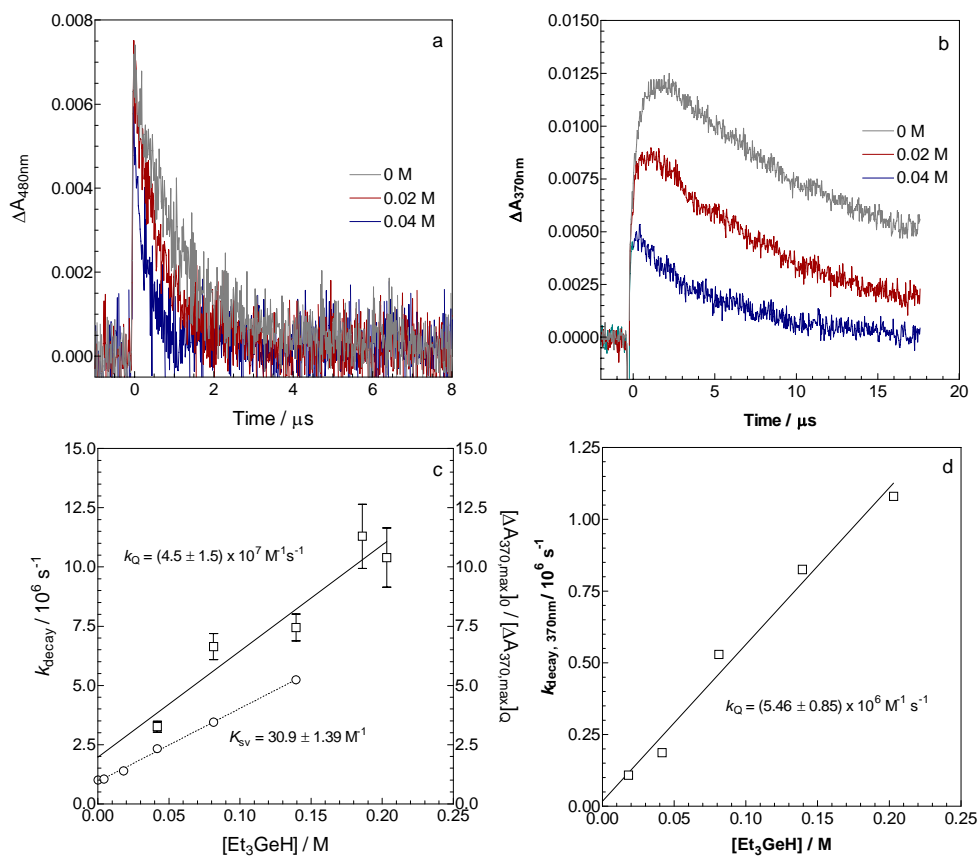
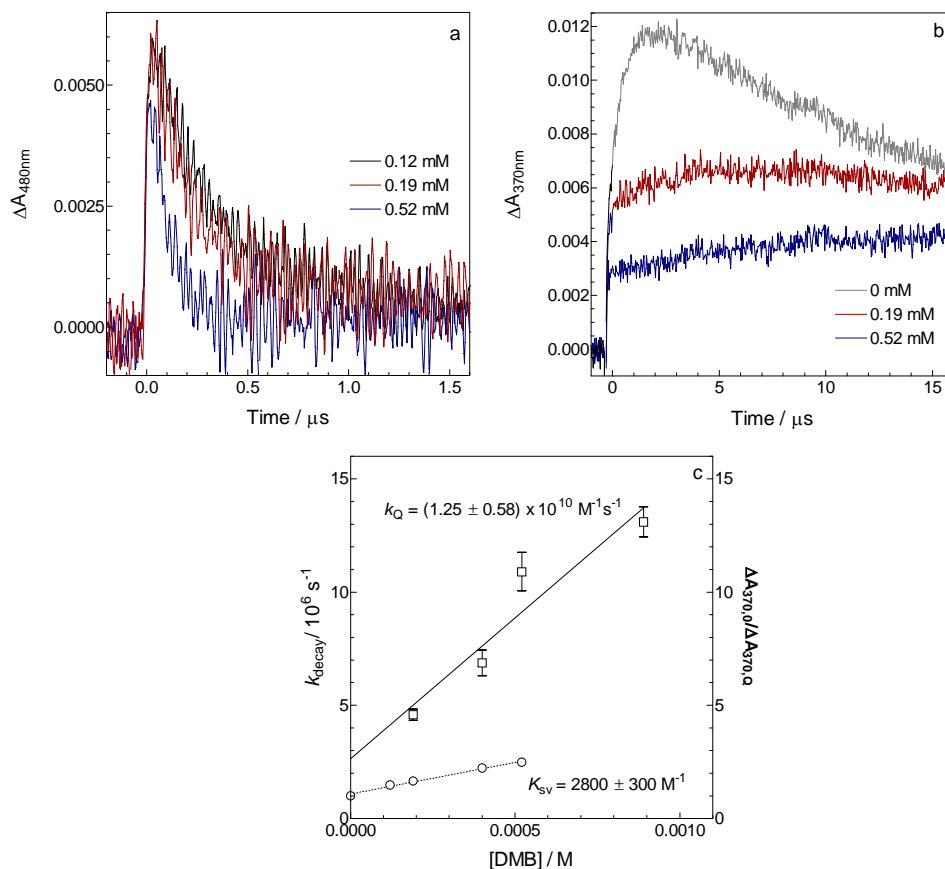


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Synthesis and Characterization of Compounds

^1H and ^{13}C NMR spectra were recorded on Bruker AV200 or AV600 spectrometers in deuterated chloroform or deuterated benzene solution and were referenced to the residual solvent proton and ^{13}C signals, respectively. Gas chromatographic (GC) separations employed a Hewlett-Packard 5890 Series II gas chromatograph equipped with a HP3396A integrator, a flame ionization detector and a DB-5 column (30m, 0.25 μm ; Chromatographic Specialties, Inc.). GC/MS experiments were carried out on a Micromass/Waters GCT GC/MS equipped with a DB-XLB column (30 m, 0.25 mm; Chromatographic Specialties, Inc.). Column chromatography was carried out using acid washed 230-400 mesh silica gel (Silicycle). Steady state photolyses were carried out in a Rayonet[®] photochemical reactor (Southern New England Ultraviolet Co.) equipped with a merry-go-round apparatus and 6 RPR-2537 lamps (254 nm).

Germanium tetrachloride (Teck-Cominco Metals Ltd.), 1,1,3,3-tetramethyldisiloxane (Gelest, Inc.), methylmagnesium bromide (3 M solution in diethyl ether; Sigma-Aldrich), and (chloromethyl)trimethylsilane (Sigma-Aldrich) were used as received from the suppliers. Hexane (EMD OmniSolv), diethyl ether (Caledon Reagent) and tetrahydrofuran (Caledon Reagent) were dried by passage through activated alumina under nitrogen using a Solv-Tek solvent purification system (Solv-Tek, Inc.). GeCl_2 -dioxane,² α -trimethylsilylacetophenone,^{3,4} 1-trimethylsilyl-2-propanone,⁵ α -bromostyrene,⁶ and 2-phenyl-1,3-butadiene (**4a**)⁴ were synthesized as described previously.

Synthesis of 2-methyl-3-phenyl-1,3-butadiene (4b). The procedure is a modification of that of Brown et al for the synthesis of **4a**.⁴ A solution of α -bromostyrene (9.15g, 0.05 mol) in anhydrous diethyl ether (30 mL) was added dropwise via addition funnel to a flame-dried 250mL 2-neck roundbottom flask (with condenser and magnetic stir-bar) containing magnesium filings

(0.055 mol, 1.35 g) and anhydrous diethyl ether (20 mL) under nitrogen and gentle reflux. The resulting brown solution was transferred to the addition funnel of a second flame-dried apparatus (identical to the first) that contained a solution of 1-trimethylsilyl-2-propanone (6.5 g, 0.05 mol) in anhydrous diethyl ether (20 mL). The Grignard reagent was added dropwise with stirring over ca 30 min and the mixture was stirred at room temperature for a further 2 hrs. It was then quenched with aqueous ammonium chloride (0.055 mol, 2.65 g in 20 mL distilled water), extracted with diethyl ether (1 x 50 mL), and finally with pentane (1 x 30 mL). The combined organic extracts were washed with water (2 x 25 mL), dried over anhydrous magnesium sulfate, and filtered. The solvent was removed on a rotary evaporator to give a viscous yellow oil (7.5 g) which was identified as 3-methyl-2-phenyl-4-(trimethylsilyl)-1-buten-3-ol on the basis of its ^1H and ^{13}C nmr spectra (purity ca. 75%; yield ~ 65 %). The alcohol was used without further purification in the next step. ^1H NMR (200 MHz, CDCl_3), δ = 0.09 (s, 11H), 1.22 (s, 3H), 1.47 (s, 1H), 4.95 (d, J = 1.4 Hz; 1H), 5.41 (d, J = 1.4 Hz; 1H), 7.33 (m, 5H); ^{13}C NMR (50 MHz, CDCl_3), δ = 0.6, 30.7, 31.6, 75.7, 112.3, 127.1, 128.6, 127.8, 129.1, 141.7. GC/MS, m/z (I) = 235 (19), 234 (32), 233 (55), 232 (40), 231 (100), 131 (63), 115 (92), 75 (100), 73 (95). Exact mass: calc. for $\text{C}_{14}\text{H}_{22}\text{OSi}$, 234.1440, found 234.1437.

The crude alcohol from above was added over a period of 30 min to a 100 mL single neck roundbottom flask containing glacial acetic acid (20 mL) saturated with sodium acetate at 60°C. The mixture was allowed to stir for further 30 min, after which it was poured into a beaker containing cold water (100 mL), neutralized with sodium carbonate and extracted with diethyl ether (1 x 25 mL). The combined organic phase was dried over anhydrous magnesium sulphate, filtered and the solvent was removed on a rotary evaporator to yield a yellow oil. This was distilled under vacuum to afford a colorless oil (3.5 g, 0.024 mol, 48%; b.p. = 47-49 °C, 0.2

mmHg⁷), which was identified as 2-methyl-3-phenyl-1,3-butadiene by comparison of its ¹H and ¹³C NMR spectra to the previously published data.^{8,9} ¹H NMR (200 MHz, CDCl₃), δ = 2.0 (s, 3H), 4.86 (s, 1H), 5.11 (m, 2H), 5.31 (s, 1H), 7.29 (m, 5H). ¹³C NMR (50 MHz, CDCl₃), δ = 21.3, 114.1, 117.1, 127.2, 128.0, 128.8, 144.2, 154.1.

Synthesis of 1,1-dimethyl-3-phenylgermacyclopent-3-ene (3a). The compound was prepared by a modification of the procedure of Manuel and coworkers.¹⁰ GeCl₂.dioxane (0.0123 mol, 2.85g) in dry THF (25 mL) was placed into a flame-dried 100 mL, 2-neck, roundbottom flask equipped with a magnetic stir bar, reflux condenser, addition funnel, and nitrogen inlet. The solution was heated to 70-75 °C while a solution of 2-phenyl-1,3-butadiene (**4a**; 2.08 g, 0.016 mol) in THF (10 mL) was added dropwise with stirring. Heating was continued for a further one hour, and then the solution was cooled and the solvent was removed by distillation. The resulting product was distilled under vacuum to afford a colorless oil identified as 1,1-dichloro-3-phenylgermacyclopent-3-ene (0.007 mol, 2.0 g, 80%; 99-100 °C, 0.01 mmHg) on the basis of its ¹H and ¹³C NMR and mass spectra (Ge-containing isotopomeric clusters are indicated with an asterisk). ¹H NMR (CDCl₃), δ = 2.48 (d, 2 H), 2.56 (d, 2 H), 6.52 (m, 1 H), 7.35 (m, 5H); ¹³C NMR (CDCl₃), δ = 27.0, 28.3, 124.0, 125.8, 128.6; MS (EI), m/z (I) = 274* (2), 205 (10), 179* (14), 131* (98), 91 (100), 77 (48), 51(18); HRMS: Exact mass: calc. for C₁₀H₁₀Cl₂Ge, 273.9371; found 273.9371.

The product from above (1.89g, 0.00695 mol) in anhydrous diethyl ether (15 mL) was placed in a 100 mL, 1-neck, roundbottom flask equipped with a magnetic stirrer, reflux condenser, addition funnel and a nitrogen inlet. The solution was cooled with an ice bath, and methylmagnesium bromide (5.8 mL (3M in ether), 0.017 mol) was added to it dropwise with stirring over 15 min. The reaction mixture was allowed to warm to room temperature and then stirred for a further 5 hrs. It was then transferred to a separatory funnel and quenched with

saturated ammonium chloride (15 mL). The aqueous fraction was extracted with diethyl ether (3 x 15 mL), and the combined ether extracts were dried over anhydrous magnesium sulfate. The solvent was removed under vacuum to give a light yellow oil, which was purified by vacuum distillation to give a colorless oil (68-70 °C (0.05 mmHg), 1.43 g, 89%) or by column distillation using a mixture of hexane and dichloromethane (2:1) as eluant. The product was identified as **3a** on the basis its ^1H and ^{13}C NMR, IR, and mass spectra (Ge isotopomeric clusters are indicated with an asterisk). Limited spectroscopic data have been reported previously for this compound by Neumann and coworkers.¹¹ IR (neat): 2972 (w), 2906 (m), 1606 (m), 1492 (m), 1444 (w), 1235 (m), 1031 (m), 828 (s) cm^{-1} ; ^1H NMR (CDCl_3), δ = 0.42 (s, 6H), 1.75 (m, 2 H), 1.88 (m, 2 H), 6.47 (m, 1 H), 7.27(m, 3H), 7.52 (m, 2H); ^{13}C NMR (CDCl_3), δ = -1.9, 20.7, 20.8, 125.9, 126.6, 128.2, 141.2, 142.3; EI-MS, m/z (I) = 234* (30), 219* (100), 129* (5), 119* (12), 89* (24), 69 (20). HRMS: Exact mass: calc. for $\text{C}_{12}\text{H}_{16}\text{Ge}$, 234.0464; found 234.0442.

Synthesis of 1,1,3-trimethyl-4-phenylgermacyclopent-3-ene (3b). GeCl_2 .dioxane (5.10g, 0.0218 mol) in anhydrous THF (35 mL) was placed in a flame-dried 100 mL, 2-neck roundbottom flask equipped with a reflux condenser, addition funnel, magnetic stir bar and a nitrogen inlet. The solution was gently refluxed and 2-methyl-3-phenyl-1,3-butadiene (**4b**; 0.024 mol, 3.4g) in THF (25 mL) was added dropwise over a period of 1 hr. The reaction mixture was further stirred for 10 min and then the THF was removed by distillation. The residue was distilled under vacuum to afford a colorless oil identified as 1,1-dichloro-3-methyl-4-phenylgermacyclopent-3-ene by ^1H and ^{13}C NMR spectroscopy (0.0194 mol, 89%; 100-101°C, 0.05 mmHg). ^1H NMR (200 MHz, CDCl_3), δ = 1.95 (s, 3H), 2.51 (d, 2H), 2.73 (d, 2H), 7.40 (m, 5H); ^{13}C NMR (50 MHz, CDCl_3), δ = 20.1, 25.6, 33.3, 67.0, 67.9, 127.0, 128.2, 132.5, 134.2, 140.3.

A solution of the dichloride from above (1.10 g, 0.0038 mol) in anhydrous diethyl ether (100 mL) was placed into a flame-dried 100 mL, two-neck roundbottom flask equipped with a magnetic stirrer and nitrogen inlet and was cooled to 5°C with an ice-bath. Methylmagnesium bromide (3.20 mL (3M in ether), 0.0096 mol) was added via a syringe through a septum to the reaction mixture over a period of 10 min. The reaction mixture was allowed to stir at room temperature for 3 hrs, and then hydrolysed with saturated aqueous ammonium chloride (10 mL). The aqueous phase was separated and extracted with diethyl ether (1 x 10 mL). The combined organic extracts were washed with distilled water (1 x 20 mL) and dried over anhydrous magnesium sulfate. Removal of the solvent on a rotary evaporator yielded a yellow oil, from which **3b** was obtained as a colorless oil by vacuum distillation (0.71 g, 0.0029 mol, 76%; 85-86 °C, 0.1 mmHg). IR (neat) 2974.5 (m) 2907.9 (s), 2887 (s), 1599 (s), 1492 (s), 1135 (s), 829 (m), 790 (s) cm^{-1} ; ^1H NMR (600 MHz, C_6D_6), δ = 0.28 (s, 6H), 1.67 (s, 2H), 1.80 (s, 3H), 1.97 (s, 2H), 7.09 (m, 4H), 7.24 (m, 1H); ^{13}C NMR (151 MHz, C_6D_6), δ = -2.4, 21.1, 27.4, 27.6, 126.2, 127.8, 128.2, 128.3, 128.6, 134.7, 137.0, 144.3; EI-MS, (m/z) (I) = 248* (58), 233* (48), 183 (24), 182 (12), 143 (28), 128 (42), 115 (38), 104* (50), 89* (100), 77 (28); HRMS: Exact mass: calc. for $\text{C}_{13}\text{H}_{18}\text{Ge}$, 248.0620; found, 248.0613.

Steady State Photolysis Experiments

Photolysis of 3a in the presence of MeOH (Figure S4). A solution of **3a** (0.0409 M), MeOH (0.2390 M) and hexamethyldisilane (0.0017 M) in cyclohexane- d_{12} was placed in an argon-filled quartz NMR tube and was sealed with a rubber septum. The solution was placed in a merry-go-round apparatus and was irradiated at 254 nm using 6 RPR-2537 lamps. The reaction mixture was photolysed for a period of 5 min (ca. 20 % conversion, see Figure S4) and the course of the

reaction was monitored at time intervals by ^1H NMR spectroscopy. The ^1H NMR spectra showed new peaks consistent with methoxydimethylgermane (**5b**)¹² in addition to those of **4a**.

Photolysis of 3a in the presence of AcOH (Figure S5). A solution of **3a** (0.05 M) and glacial acetic acid (0.25 M) in cyclohexane- d_{12} was placed in a quartz NMR tube, sealed with a rubber septum, and deoxygenated with a stream of dry argon. The solution was placed in a merry-go-round apparatus and was irradiated at 254 nm using 6 RPR-2537 lamps. The reaction mixture was photolysed for a period of 16 minutes (ca. 60 % conversion, see Figure S5), during which the course of the reaction was monitored periodically by ^1H NMR spectroscopy. Acetoxydimethylgermane was identified as the main product by comparison to the reported ^1H NMR spectrum.¹³ The chemical yields of **5a** and **4a** after 60% conversion were estimated as 91% and 96%, respectively.

Photolysis of 3a in the presence of DMB. A solution of **3a** (0.03 M), 2,3-dimethylbutadiene (0.05 M) and n-dodecane (0.003 M) in dry hexane was placed in a quartz photolysis tube, sealed with a rubber septum, and was deoxygenated with a stream of dry argon. The solution was placed in a merry-go-round apparatus and was irradiated at 254 nm using 6 RPR-2537 lamps. The reaction mixture was photolysed for a period of 12 minutes (ca. 60 % conversion), with periodic monitoring by GC-FID and GC-MS. The gas chromatogram indicated the presence of two major products with retention times of 4.32 and 5.12 minutes (n-dodecane, 6.65 min; **3a**, 9.97 min), in roughly equal yields. The two peaks were identified as **4a** and **1c** by GC-MS, and confirmed by spiking the mixture with small amounts of authentic samples of the two compounds.¹⁴ Two additional products (with retention times of 6.52 and 6.62 minutes) were also formed in yields of 3-5% each, but were not identified.

Photolysis of 3b in the presence of AcOH (Figure S6). A solution of **3b** (0.05 M), glacial acetic acid (0.26 M), and hexamethyldisilane (0.02 M) in cyclohexane- d_{12} was placed in a quartz NMR tube, sealed with a rubber septum, and deoxygenated with a stream of dry argon. The solution was placed in a merry-go-round apparatus and was irradiated at 254 nm using 6 RPR-2537 lamps. The reaction mixture was photolyzed for a period of 16 minutes (ca. 30% conversion), monitoring periodically by ^1H NMR spectroscopy. Figure S6 shows the mixture before and after irradiation to ca. 30% conversion. The chemical yields of **5a** and **4b** after 30% conversion were estimated as 99% and 98%, respectively.

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