

Supporting Information

Competing Germene and Germylene Extrusion from Photolysis of 1,1-Diarylgermacyclobutanes. Substituent Effects on Germene Reactivity.

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- Synthesis and Characterization of Compounds** S3
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- Figure S1.** Concentration vs. time plots, from parallel photolysis of 0.041 M solutions of **4**, **5**, and **14a** in cyclohexane-*d*₁₂ containing ca. 0.2 M MeOH and hexamethyldisilane (ca. 5 mM) as internal integration standard. (a) [**14a**], [**4**], and [**5**] vs. time (slopes: **14a**, -0.0136 ± 0.0005 ; **4**, -0.0056 ± 0.0006 ; **5**, -0.0047 ± 0.0004). (b) [product] vs. time from photolysis of **14a** (slopes: **13a**, 0.0098 ± 0.0004 from Ge-H, 0.0111 ± 0.0004 from OMe; DMB, 0.0130 ± 0.0003). (c) [product] vs. time from photolysis of **4** (slopes: C₂H₄, 0.0021 ± 0.0001 ; **13b**, 0.00188 ± 0.00004 from Ge-H; C₃H₆, 0.00213 ± 0.00004 ; **12b**, 0.00276 ± 0.00002). (d) [product] vs. time from photolysis of **5** (slopes: C₂H₄, 0.00108 ± 0.00006 ; **13c**, 0.00221 ± 0.00004 from Ge-H, 0.00245 ± 0.00010 from OMe; C₃H₆, 0.00254 ± 0.00004 ; **12c**, 0.00145 ± 0.00010). Errors are quoted as $\pm 2\sigma$ from linear least squares analysis of the data. S16
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Synthesis and Characterization of Compounds

^1H NMR spectra were recorded on Bruker AV200, DRX500 or AV600 NMR spectrometers in CDCl_3 , benzene- d_6 or cyclohexane- d_{12} solution and are reported in parts per million (δ) downfield from tetramethylsilane using the residual solvent-proton resonances as the internal standard. 125 MHz ^{13}C and 188 MHz ^{19}F NMR spectra were recorded on the DRX500 and AV200 spectrometers, respectively, and are referenced relative to tetramethylsilane and (external) CFCl_3 , respectively. Ultraviolet absorption spectra were recorded on a Varian Cary 50 UV-Visible spectrophotometer. Infrared spectra were recorded on a BioRad FTS-40 FTIR spectrophotometer and are reported in wavenumbers (cm^{-1}). Elemental analyses were performed by Guelph Chemical Laboratories, or on a Thermo FlashEA 1112 elemental analyzer using methionine as calibrant. Melting points were determined using a Mettler FP82 hot stage (controlled by a Mettler FP80 central processor) mounted on a microscope and are uncorrected. Analytical gas chromatographic analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector, conventional heated splitless injector (220 °C), a Hewlett-Packard 3396A recording integrator and one of the following fused silica capillary columns: (a) SPB-1 (20 m x 0.25 mm; 0.25 μm ; Supelco, Inc.); (b) DB-5 (5 m x 0.53 mm; 1.5 μm ; J & W Scientific). Radial chromatographic separations employed a Chromatotron[®] (Harrison Research, Inc.), 4-mm silica gel 60 thick-layer plates, and hexane as eluant. Column chromatography was carried out using acid washed 230-400 mesh silica gel (Silicycle).

GC/MS analyses were carried out on a Hewlett-Packard 5890 gas chromatograph equipped with a HP-5971A mass selective detector and a DB-1 fused silica capillary column (DB-5; 30m x 0.25mm ID with 0.25 micron film; Chromatographic Specialties, Inc.), a Varian Saturn 2200 GC/MS/MS system equipped with a VF-5ms capillary column (30 m x 0.25 mm; 0.25 μm ; Varian, Inc.), or a Micromass/Waters GCT GC/MS equipped with a DB-XLB column (30 m,

0.25 mm; Chromatographic Specialties, Inc.); all employed (70 eV) electron impact ionization. High resolution exact masses were determined on the latter instrument employing a mass of 12.000000 for carbon-12. For all the compounds studied in this work, mass spectra recorded on the Hewlett-Packard ('HP') and Varian ('VS') instruments were quite similar to one another, but generally quite different from those recorded on the Micromass/Waters ('GCT') instrument. We thus report both spectra for several of the compounds described below; m/z values marked with * indicate ions containing ^{74}Ge .

2,3-Dimethylbutadiene and acetone were obtained from Sigma-Aldrich Chemical Co. and were distilled before use. 1,3-Dibromopropane, 4-bromobenzotrifluoride, 3,5-bis(trifluoromethyl)bromobenzene, and 1-bromo-3-phenoxypropane were used as received from Sigma-Aldrich Chemical Co. Chloroform- d , cyclohexane- d_{12} , and benzene- d_6 were used as received from Cambridge Isotope Labs. Germanium tetrachloride (Gelest, Inc. or Teck-Cominco Metals, Ltd.) and methylgermanium trichloride (Gelest, Inc.) were used as received from the suppliers. 1,1-Diphenylgermacyclobutane (**2**)¹, GeCl_2 -dioxane,² 1-dichloro-3,4-dimethylgermacyclopent-3-ene,² and 3,4-dimethyl-1,1-diphenylgermacyclopent-3-ene (**14a**)² were prepared and purified as previously reported. Cyclopropane was prepared by the method of Gragson and coworkers.³

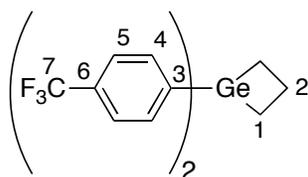
All synthetic manipulations were carried out in flame-dried glassware under an atmosphere of dry argon or nitrogen.

1,1-Bis(4-(trifluoromethyl)phenyl)germacyclobutane (4). Freshly ground magnesium turnings (2.43 g, 0.10 g-atom) and anhydrous ether (80 mL) were placed in a two-neck 250 mL round-bottom flask fitted with an addition funnel and condenser under a nitrogen atmosphere. A solution of 4-bromobenzotrifluoride (10.49 g, 0.0466 mol) in anhydrous ether (50 mL) was added dropwise with vigorous stirring over a period of 3 hours and then left to stir for a further

12 hours at room temperature. Germanium tetrachloride (5.00 g, 0.0233 mol) and dry ether (100 mL) were placed in a two-neck 500 mL roundbottom flask fitted with a 250 mL addition funnel under nitrogen, and the apparatus was placed in a dry ice/isopropanol bath. The solution of the freshly made Grignard reagent from above was transferred to the addition funnel and added dropwise with vigorous stirring over a period of 3 hours. The resulting solution was allowed to warm slowly to room temperature and was then left to stir for 12 hours. The reaction mixture was filtered, and the solvent was removed on the rotary evaporator to yield an orange oil (12.27 g). Analysis of the oil by GC (column b) showed three major products with retention times of 13.7 minutes, 15.8 minutes and 17.6 minutes, in an area ratio of 1:6:1. The oil was used without further treatment in the next step.

The following procedure is a modification of the method of Bickelhaupt and co-workers.⁴ Freshly ground magnesium turnings (28.34 g, 1.17 g-atom) and anhydrous ether (250 mL) were added to a two-neck 500 mL roundbottom flask fitted with an addition funnel and condenser under a nitrogen atmosphere, and a small crystal of iodine was added. A solution of 1,3-dibromopropane (11.83 mL, 0.116 mol) in anhydrous ether (60 mL) was added dropwise with vigorous stirring over a period of 2 hours and the reaction mixture was left to stir for a further 3 hours. The orange oil from the preceding step was dissolved in a small portion of anhydrous ether and added rapidly to the reaction mixture, which was then stirred at room temperature for 12 hours. The resulting mixture was decanted into a large flask and slowly quenched with distilled water (100 mL). The organic layer was separated and washed with water (25 mL), saturated aqueous ammonium chloride (50 mL), and again with water (25 mL), and then dried with anhydrous magnesium sulfate. The solvent was removed on the rotary evaporator to yield a golden oil (10.95 g). Subsequent purification was accomplished using radial chromatography and silica gel column chromatography with hexane as the eluting solvent, followed by three recrystallizations from methanol. The latter afforded the product as colorless needles (2.95 g,

0.0073 mol, 31%; m.p. 46-47 °C) in > 99% purity as determined by GC analysis (column a). It was identified as 1,1-bis(4-(trifluoromethyl)phenyl)germacyclobutane (**4**) on the basis of the following spectroscopic and analytical data. ^1H NMR (CDCl_3 , 500 MHz): δ = 2.059 (t, J = 8.2 Hz, 4H, H-1), 2.450 (quint, J = 8.2 Hz, 2H, H-2), 7.666 (d, J = 7.6 Hz, 4H, H-4), 7.704 (d, J = 7.6 Hz, 4H, H-5). ^{13}C NMR (CDCl_3 , 125 MHz): δ = 20.9, 21.6, 124.3 (q, J = 272 Hz, C-7), 125.1 (C-5), 131.7 (q, J = 32 Hz, C-6), 134.4 (C-4), 143.1 (C-3). ^{19}F NMR (CDCl_3 , 188 MHz): δ = -63.2 ppm (s). IR (KBr, cm^{-1}): 2933 (m), 1929 (w), 1607 (m), 1395 (m), 1325 (s), 1165 (s), 1125 (s), 1101 (m), 1056 (s), 1017 (m), 826 (m), 689 (m), 597 (w), 565 (w), 494 (w), 446 (w). Mass spectra: (GCT, m/z (%)): 406 (20), 378 (50), 362 (45), 343 (8), 309 (10), 271 (85), 252 (85), 251 (50), 219 (95), 140 (100). HRMS calculated for $\text{C}_{17}\text{H}_{14}\text{F}_6\text{Ge}$ ($[\text{M}]^+$), 406.0211; found 406.0210. Analysis, calc. for $\text{C}_{17}\text{H}_{14}\text{F}_6\text{Ge}$: C, 50.43%, H, 3.49%; found: C, 50.73%, H, 3.41%.

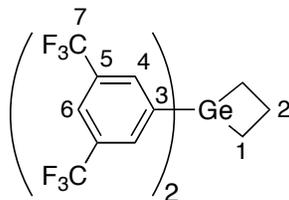


1,1-Bis[3,5-bis(trifluoromethyl)phenyl]germacyclobutane (5) was prepared in an analogous manner to **4**. Freshly ground magnesium turnings (2.46 g, 0.101 g-atom) and anhydrous ether (350 mL) were placed in a two-neck 500 mL roundbottom flask fitted with an addition funnel and condenser under a nitrogen atmosphere. A solution of 3,5-bis(trifluoromethyl)bromobenzene (13.65 g, 0.0466 mol) in anhydrous ether (60 mL) was added dropwise with vigorous stirring over a period of 3 hours, and the resulting mixture was then left to stir for 12 hours at room temperature. Germanium tetrachloride (5.00 g, 0.0233 mol) and anhydrous ether (150 mL) were placed in a two-neck 500 mL roundbottom flask fitted with a 250 mL addition funnel under nitrogen, and the apparatus was placed in a dry ice/isopropanol bath. The freshly made Grignard reagent was transferred to the addition funnel and added

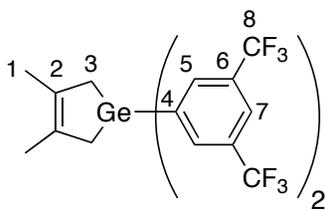
dropwise with vigorous stirring over a period of 3 hours, and the resulting mixture was allowed to warm slowly to room temperature and then left to stir for 12 hours. The mixture was filtered and the solvent was removed on the rotary evaporator to yield a brown oil (13.1 g). Analysis of the oil by GC (column b) showed three major products with retention times of 3.8 minutes, 5.8 minutes and 8.0 minutes in an area ratio of 1:4:1. The oil was used without further treatment in the next step.

Freshly ground magnesium turnings (28.70 g, 1.18 g-atom) and anhydrous ether (300 mL) were placed in a two-neck roundbottom flask fitted with a condenser and 125 mL addition funnel and under a nitrogen atmosphere. A small crystal of iodine was added, and then a solution of 1,3-dibromopropane (11.83 mL, 0.116 mol) in anhydrous ether (60 mL) was added dropwise with vigorous stirring over a period of 1½ h. The reaction mixture was left to stir for an additional 3 h. The brown oil from the preceding paragraph was dissolved in a small portion of anhydrous ether and added rapidly to the reaction mixture, which was then stirred for 12 hours at room temperature. Workup as before yielded a yellow oil (13.03 g), which was purified by radial chromatography and silica gel column chromatography followed by three recrystallizations from methanol to yield colorless needles (2.61 g, 0.0048 mol, 21%; m.p. 64-64.5°C) in > 99% purity as determined by GC analysis (column a). The compound was identified as 1,1-bis[3,5-bis(trifluoromethyl)phenyl]germacyclobutane (**5**) on the basis of the following spectroscopic and analytical data. ¹H NMR (CDCl₃, 500 MHz): δ = 2.177 (t, J = 8.2 Hz, 2H), 2.502 (quint, J = 8.2 Hz, 4H), 7.959 (s, 2H), 7.978 (s, 4H). ¹³C NMR (CDCl₃, 125 MHz): δ = 21.5, 21.5, 123.5 (q, J = 273 Hz), 123.9, 131.9 (q, J = 33 Hz), 133.8, 140.6. ¹⁹F NMR (CDCl₃, 188 MHz): δ = -63.1 (s). IR (KBr, cm⁻¹): 2911 (w), 1620 (w), 1359 (s), 1282 (s), 1174 (s), 1125 (s), 920 (w), 896 (m), 840 (m), 706 (m), 682 (s), 567 (w), 500 (w), 449 (w), 429 (w). MS: (EI, m/z (%)) = 542 (15), 523 (25), 514(75), 500 (25), 388 (100), 387 (80), 287 (30), 208

(80), 194 (50), 175 (30), 155 (92). HRMS: calc. for $C_{19}H_{12}F_{12}Ge$ ($[M]^+$) = 541.9959; found, 542.0007. Elemental analysis: calc. for $C_{19}H_{12}F_{12}Ge$, C 42.19%, H 1.89%; found, C 42.08%, H 2.24%.



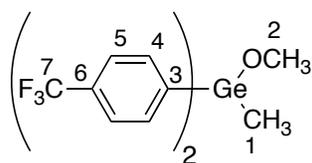
3,4-Dimethyl-1,1-bis[3,5-bis(trifluoromethyl)phenyl]germacyclopent-3-ene (14c) was prepared from 1,1-dichloro-3,4-dimethylgermacyclopent-3-ene (2.2 g, 9.7 mmol) and bis-3,5-(trifluoromethyl)phenyl magnesium bromide [from 1-bromo-bis-3,5-(trifluoromethyl)benzene (7.8 g, 26.5 mmol) and magnesium (0.71 g, 0.0295 g-atom) in ether] by an analogous method to that used for the preparation of other 1,1-diaryl-3,4-dimethylgermacyclopent-3-ene derivatives,^{2,5} and was purified by column chromatography (silica gel, hexanes) followed by multiple recrystallizations from hexanes. The compound was obtained as colorless needles (2.3 g, 4.0 mmol, 41%; mp 76.6-77.4 °C) and was identified on the basis of the following spectroscopic and analytical data: 1H NMR ($CDCl_3$, 600 MHz): δ = 1.84 (s, 6H, H-1), 2.15 (s, 4H, H-3), 7.89 (s, 4H, H-5), 7.92 (s, 2H, H-7); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 19.39 (C-1), 25.30 (C-3), 123.47 (q, J = 273 Hz, C-8), 123.60 (C-7), 130.77 (C-2), 131.70 (q, J = 33 Hz, C-6), 133.98 (C-5), 140.10 (C-4); IR (film, cm^{-1}): 2987 (m), 2927 (m), 1832 (w), 1616 (w), 1445 (w), 1357 (s), 1280 (s), 1167 (s), 1127 (s), 984 (w), 894 (m); MS: (EI, m/z (%)) = 582.0* (28), 563.0* (6), 388.0 (100), 369.0* (10), 286.9* (15), 194.0 (48); HRMS: calc. for $C_{22}H_{16}F_{12}Ge$ ($[M]^+$) = 582.0276; found, 582.0298. Elemental analysis: calc. for $C_{22}H_{16}F_{12}Ge$, C 45.48%, H 2.78%; found, C 45.83%, H 2.39%.



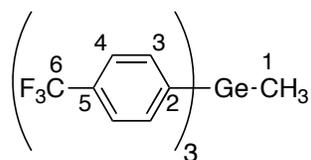
Methoxy(methyl)bis(4-trifluoromethylphenyl)germane (12b). (a) *Chloro(methyl)bis(4-trifluoromethylphenyl)germane*. In a 50 mL two-neck round-bottom flask fitted with condenser, addition funnel, magnetic stirrer, and nitrogen inlet were placed magnesium (0.65 g, 0.0267 g-atom) and dry ether (10 mL). A solution of 4-bromobenzotrifluoride (4.18 g, 18.5 mmol) in dry ether (25 mL) was placed in the addition funnel and ca. 10% of the solution was added to the round-bottom flask rapidly, followed by 2-3 drops of 1,2-dibromoethane, with vigorous stirring. The solution began to turn red after a few minutes, at which point it was cooled to 0 °C and the remainder of the aryl halide was added drop-wise over a period of 1.5 h. The resulting reddish-brown solution was allowed to warm to room temperature and was then stirred for 12 h. A 100 mL two neck round-bottom flask, fitted with a condenser and an addition funnel, was charged with methyltrichlorogermane (1.02 g, 5.3 mmol) and dry ether (6 mL). The Grignard reagent was cannulated into the addition funnel and added dropwise (at 0 °C) over a period of 3 h. The resulting reddish-orange solution was allowed to warm to room temperature and was then stirred for 16 h. The solvent was removed under vacuum to yield a semi-solid, which was extracted with two 25 mL portions of dry hexane, removing the supernatant with a cannula. The combined hexane extracts were concentrated under vacuum (0.2 mm Hg) for 5 h to yield a yellow oil (2.53 g). The ^1H NMR spectrum indicated the material to consist of two main Ge-containing components in a ca. 1:1 ratio, which were tentatively identified as chloro(methyl)bis(4-trifluoromethylphenyl)germane [^1H NMR (CDCl_3 , 200 MHz), $\delta = 1.34$ (s, 3H), 7.71 (s, 8H)] and methyltris(4-trifluoromethylphenyl)germane [^1H NMR (CDCl_3 , 200 MHz): $\delta = 1.007$ (s, 3H, H-1), 7.570 (d, $J = 8.0$ Hz, 6H, H-4), 7.642 (d, $J = 7.8$ Hz, 6H, H-3)]. The second compound was

characterized further at the conclusion of the next step.

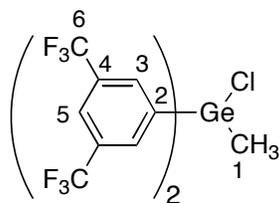
(b) *Methoxy(methyl)bis(4-trifluoromethylphenyl)germane* (**12b**). The oil obtained in step (a) was dissolved in dry benzene (18 mL) in a 50 mL, two-neck round-bottom flask fitted with a condenser and magnetic stirrer, and dry methanol (1.3 mL, 32.1 mmol) and triethylamine (1.1 mL, 7.9 mmol) were added. The resulting solution was stirred at 80 °C for 17 h. The solvent was removed under vacuum, hexane (25 mL) was added to cause precipitation of salts, and the supernatant was cannulated. This was repeated with a second 15 mL portion of dry hexane. The combined extracts were concentrated to yield a yellow semi-solid (2.26 g.). The material was fractionated using a Kugelrohr apparatus under vacuum (93 °C, 0.2 mm Hg), affording methoxy(methyl)bis(4-trifluoromethylphenyl)germane (**12b**, 0.40 g, 19%) as a colorless oil in ca. 80% purity, as estimated by ¹H NMR spectroscopy. The compound was identified on the basis of the following spectroscopic and analytical data (¹H and ¹³C NMR spectral assignments for aromatic protons and carbons were determined using HSQC and HMBC experiments): ¹H NMR (CDCl₃, 600 MHz), δ = 0.949 (s, 3H, H-1), 3.557 (s, 3H, H-2), 7.696 (d, *J* = 8.4 Hz, 4H, H-5), 7.705 (d, *J* = 8.4 Hz, 4H, H-4); ¹H NMR (C₆D₁₂, 500 MHz), δ = 0.81 ppm (s, 3H), 3.49 ppm (s, 3H); ¹³C NMR (CDCl₃, 150 MHz), δ = -3.84 (C-1), 53.30 (C-2), 124.10 (q, *J* = 271 Hz, C-7), 125.25 (C-5), 132.39 (q, *J* = 33 Hz, C-6), 134.18 (C-4), 140.49 (C-3); MS (GCT) (*m/z* (I)) = 395* (100) ([M - Me]⁺), 379* (18), 365* (78), 235* (18), 219* (13), 126* (20), 107* (12); HRMS, calc. for C₁₅H₁₁F₆GeO ([M - Me]⁺) = 394.9926; found, 394.9909. The compound decomposed slowly over the course of several days' storage as the neat liquid at ca. 5 °C, and GC/MS analysis required use of reduced injector temperatures (160 °C) to minimize thermal decomposition upon injection.



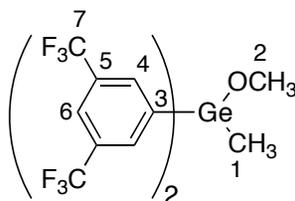
The second (higher-boiling) fraction from the distillation (1.75 g) was dissolved in a small amount of ether and allowed to crystallize, affording pale yellow prisms (m.p. 103.5-104 °C) that were identified as methyltris(4-trifluoromethylphenyl)germane on the basis of the following data (see (a) for ^1H NMR spectrum): ^{13}C NMR (CDCl_3 , 50 MHz): $\delta = -4.22$ (C-1), 124.14 (q, $J = 271$ Hz, C-6), 125.21 (q, $J = 3.5$ Hz, C-4), 131.78 (q, $J = 32.5$ Hz, C-5), 134.83 (C-3), 141.34 (C-2); MS (GCT) (m/z (I)) = 509* (100) ($[\text{M-Me}]^+$), 480 (42), 379* (17), 271 (34), 257* (65), 224* (21), 219* (13), 152* (4), 145* (18), 126* (22), 97 (27), 83 (32), 69 (42), 57 (65), 43 (72); HRMS, calc. for $\text{C}_{21}\text{H}_{12}\text{F}_9\text{Ge}$ ($[\text{M-Me}]^+$), 509.0007; found, 509.0018.



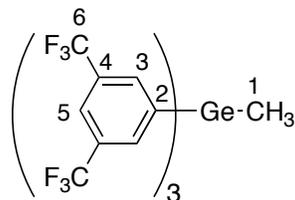
Methoxy(methyl)bis[3,5-bis(trifluoromethyl)phenyl]germane (12c). (a) *Chloro(methyl)bis[3,5-bis(trifluoromethyl)phenyl]germane* was prepared by stirring methylgermanium trichloride (0.51 g, 2.6 mmol) with 3,5-bis(trifluoromethyl)phenylmagnesium bromide (from 1-bromo-3,5-bis(trifluoromethyl)benzene (2.72 g, 9.3 mmol) and magnesium (0.36 g, 0.0148 g-atom), as described above) in dry ether (ca. 30 mL) at room temperature for 16 h. The solvent was removed under vacuum to yield a semi-solid, which was extracted with two 20 mL portions of dry hexane, removing the supernatant with a cannula. The combined hexane extracts were concentrated under vacuum (0.2 mm Hg) for 5 h to yield a yellow-orange semi-solid (1.60 g). ^1H NMR and GC/MS analysis indicated the material to consist of two main germanium-containing components in a ca. 1:1 ratio, which were tentatively identified as chloro(methyl)bis[3,5-bis(trifluoromethyl)phenyl]germane [^1H NMR (CDCl_3 , 200 MHz), $\delta = 1.45$ (s, 3H), 8.00 (s, 6H, H-3,5)] and methyltris[3,5-bis(trifluoromethyl)phenyl]germane [^1H NMR (CDCl_3 , 200 MHz): $\delta = 1.18$ (s, 3H, H-1), 7.84 (s, 6H, H-3), 8.00 (s, 3H, H-5)]. The second compound was characterized further at the conclusion of the next step.



(b) *Methoxy(methyl-bis[3,5-bis(trifluoromethyl)phenyl]germane (12c)*. The material (1.42 g) obtained in step (a) was dissolved in dry benzene (12 mL) in a 25-mL, two-neck round-bottom flask fitted with a condenser and magnetic stirrer, and dry methanol (1 mL, 24.7 mmol) and triethylamine (0.5 mL, 3.6 mmol) were added. The resulting solution was stirred at 80 °C for 17 h. The solvent was removed under vacuum, hexane (15 mL) was added to cause precipitation of salts, and the supernatant solution was removed with a cannula. This was repeated with a second 15 mL portion of dry hexane. The combined extracts were concentrated under vacuum to yield a yellow semi-solid (1.05 g). The material was fractionated using a Kugelrohr apparatus under vacuum (85 °C, 0.05 mm Hg), affording methoxy(methyl-bis[3,5-bis(trifluoromethyl)phenyl]germane (**12c**, 0.21 g, 20%) as a colorless oil in ca. 85% purity, as estimated by ^1H NMR spectroscopy. The compound was identified on the basis of the following spectroscopic and analytical data (^1H and ^{13}C NMR spectral assignments for aromatic protons and aromatic/quaternary carbons were determined using HSQC and HMBC experiments): ^1H NMR (CDCl_3 , 600 MHz), δ = 1.05 ppm (s, 3H, H-1), 3.58 (s, 3H, H-2), 7.98 (s, 6H, H-4,6); ^1H NMR (C_6D_{12} , 500 MHz), δ = 0.92 ppm (s, 3H), 3.53 ppm (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz), δ = -3.90 ppm (C-1), 53.39 (C-2), 123.33 (q, J = 271.50 Hz, C-7), 124.59 (C-6), 132.03 (q, J = 33 Hz, C-5), 133.47 (C-4), 138.51 (C-3); MS (GCT) (m/z (I)) = 531* (82) ($[\text{M} - \text{Me}]^+$), 515* (30), 501* (100), 287* (15), 195 (21), 175 (13); HRMS, calc. for $\text{C}_{17}\text{H}_9\text{F}_{12}\text{GeO}$ ($[\text{M} - \text{Me}]^+$) = 530.9673; found, 530.9680. The compound decomposed slowly over the course of several days' storage as the neat liquid at ca. 5 °C, and GC/MS analysis required use of reduced injector temperatures (160 °C) to minimize thermal decomposition upon injection.



The second (higher-boiling) fraction from the distillation (0.75 g) was dissolved in a small amount of 1:1 ether:hexane and allowed to crystallize, affording pale yellow plates (m.p. 118.7 °C – 119.3 °C) which were identified as methyltris[3,5-bis(trifluoromethyl)phenyl]germane on the basis of the following data (see (a) for ^1H NMR spectrum): ^{13}C NMR (CDCl_3 , 50 MHz): $\delta = -3.84$ (C-1), 123.20 (q, $J = 271$ Hz, C-6), 124.49 (C-5), 132.33 (q, $J = 33$ Hz, C-4), 134.02 (C-3), 137.84 (C-2); MS (GCT) (m/z (I)) = 713* (100) ($[\text{M-Me}]^+$), 515* (22), 407 (13), 388 (13), 319* (10), 287* (7), 213 (9), 194 (38), 144 (14), 125 (8); HRMS, calc. for $\text{C}_{24}\text{H}_9\text{F}_{18}\text{Ge}$ ($[\text{M-Me}]^+$), 712.9629; found, 712.9601.



Steady-State Photolysis Experiments

Steady-state photolysis experiments were carried out in cyclohexane- d_{12} solution using a Rayonet Photochemical Reactor (Southern New England Ultraviolet Co.) equipped with two or six RPR-2537 lamps (254nm). Photolysis solutions were contained in 5 x 75 mm quartz NMR tubes, which were sealed with rubber septa and deoxygenated with a stream of dry argon. The progress of the reactions was monitored by ^1H NMR spectroscopy and by GC/MS. Product yields were calculated relative to consumed germacyclobutane from the slopes of concentration vs. plots constructed from NMR data recorded at selected time intervals over the 0-30% conversion range. Errors are quoted as $\pm 2\sigma$ from linear least squares analysis of the data.

(a) *Photolysis of 4 and 5 in the presence of MeOH.* Photoproducts were identified by NMR spectroscopy, by spiking the crude photolysates after ca. 50% conversion of starting material with small amounts of the appropriate authentic samples. Additional confirmation of the identities of **12b,c** was obtained by comparison of GC/MS data for the crude photolysates with those for the authentic samples.

Bis(4-(trifluoromethyl)phenyl)methoxygermane (13b) was identified in the photolysis mixture from **4** (0.04 M in C₆D₁₂ containing 0.3 M MeOH) by ¹H NMR spectroscopy, after spiking the photolysate with a small amount of the reaction mixture obtained from photolysis of a deoxygenated solution of 1,1-bis[4-(trifluoromethyl)phenyl]-3,4-dimethylgermacyclopent-3-ene (**14b**; 0.02 M) in cyclohexane-*d*₁₂ containing MeOH (0.3 M), as previously reported.⁵

Similarly, **bis(3,5-bis(trifluoromethyl)phenyl)methoxygermane (13c)** was identified in the photolysis mixture from **5** (0.04 M in C₆D₁₂ containing 0.3 M MeOH) by ¹H NMR spectroscopy, after spiking the photolysate with a small amount of the reaction mixture obtained from photolysis of a deoxygenated solution of 1,1-bis[3,5-bis(trifluoromethyl)phenyl]-3,4-dimethylgermacyclopent-3-ene (**14c**; 0.05 M) in cyclohexane-*d*₁₂ containing MeOH (0.2 M) to ca. 20% conversion. The photolysis of **14c** affords 2,3-dimethyl-1,3-butadiene (DMB) in 88% yield and a second product (84%) identifiable as bis(3,5-bis(trifluoromethyl)phenyl)methoxygermane (**13c**): ¹H NMR (C₆D₁₂), δ = 3.63 (s, 3H, OMe), 6.32 (s, 1H, GeH), 7.95 (s, 2H, *p*-H), 8.00 (s, 4H, *o*-H). The compound could not be detected by GC/MS, presumably owing to facile thermal decomposition.⁵

Quantum yields for the formation of **12b,c** and **13b,c** were determined from the slopes of concentration vs. time plots, constructed from ¹H NMR data obtained by merry-go-round photolyses of deoxygenated solutions of **14a**, **4**, and **5** (0.04 M) in cyclohexane-*d*₁₂ containing MeOH (0.20 M) and hexamethyldisilane (~ 5 mM) as internal standard, relative to that for the

formation of **13a** from photolysis of **14a** ($\Phi_{13a} = 0.55 \pm 0.07$).⁶ The quantum yields for the formation of **13c** from **14c** ($\Phi_{13c} = 0.47 \pm 0.09$) were determined in similar fashion, using the photolysis of **14a** as actinometer. Concentrations of the germylene insertion products **13a-c** were calculated using the OMe proton integrals in all cases but the photolysis of **4**, where the Ge-H proton integral had to be used because of overlap between the OMe singlet in **13b** and the O-H proton resonance due to MeOH; in this case, a correction factor of 0.88 was applied to the slope of the [**13b**] vs. time plot in order to correct for a systematic underestimation of the Ge-H integral relative to the OMe proton integral in the NMR spectra of **13b** and **13c** (area ratio $\sim 0.88:3$ under the conditions employed for recording these spectra), due to the longer relaxation time associated with Ge-H protons compared to C-H protons. Concentration vs. time plots are shown in Figures S1–S3.

(b) Photolysis of 2 in the presence of AcOH. Product yields were determined relative to consumed **2** from the slopes of concentration vs. time plots, constructed from ¹H NMR spectra recorded for a 0.04 M solution of **2** in C₆D₁₂ containing AcOH (0.05 M) and hexamethyldisilane (1.5 mM) as internal integration standard, over the 0–5% conversion range in **2**. Figure S4 shows the concentration vs. time plots and the ¹H NMR spectrum of the mixture at the highest conversion studied. The only product detectable by GC/MS analysis of the mixture is **15a** (m/z (I) = 287* (100; M⁺-Me), 243* (15), 225* (18), 183* (8), 151 (5), 91 (5), 77 (10), 51 (15), 43 (8).

(c) Photolysis of 2 in the presence of DMB. ¹H NMR spectra recorded before and after photolysis of a 0.05 M solution of **2** in C₆D₁₂ solution containing 0.04 M DMB to ca. 25% conversion of germacyclobutane are shown in Figure S5. Compounds **14a** and **17a** were identified by ¹H NMR spectroscopy, after spiking the crude photolysis mixtures with authentic samples.

Figure S1. Concentration vs. time plots, from parallel photolysis of 0.041 M solutions of **4**, **5**, and **14a** in cyclohexane- d_{12} containing ca. 0.2 M MeOH and hexamethyldisilane (ca. 5 mM) as internal integration standard. (a) [**14a**], [**4**], and [**5**] vs. time (slopes: **14a**, -0.0136 ± 0.0005 ; **4**, -0.0056 ± 0.0006 ; **5**, -0.0047 ± 0.0004). (b) [product] vs. time from photolysis of **14a** (slopes: **13a**, 0.0098 ± 0.0004 from Ge-H, 0.0111 ± 0.0004 from OMe; DMB, 0.0130 ± 0.0003). (c) [product] vs. time from photolysis of **4** (slopes: C_2H_4 , 0.0021 ± 0.0001 ; **13b**, 0.00188 ± 0.00004 from Ge-H; C_3H_6 , 0.00213 ± 0.00004 ; **12b**, 0.00276 ± 0.00002). (d) [product] vs. time from photolysis of **5** (slopes: C_2H_4 , 0.00108 ± 0.00006 ; **13c**, 0.00221 ± 0.00004 from Ge-H, 0.00245 ± 0.00010 from OMe; C_3H_6 , 0.00254 ± 0.00004 ; **12c**, 0.00145 ± 0.00010). Errors are quoted as $\pm 2\sigma$ from linear least squares analysis of the data.

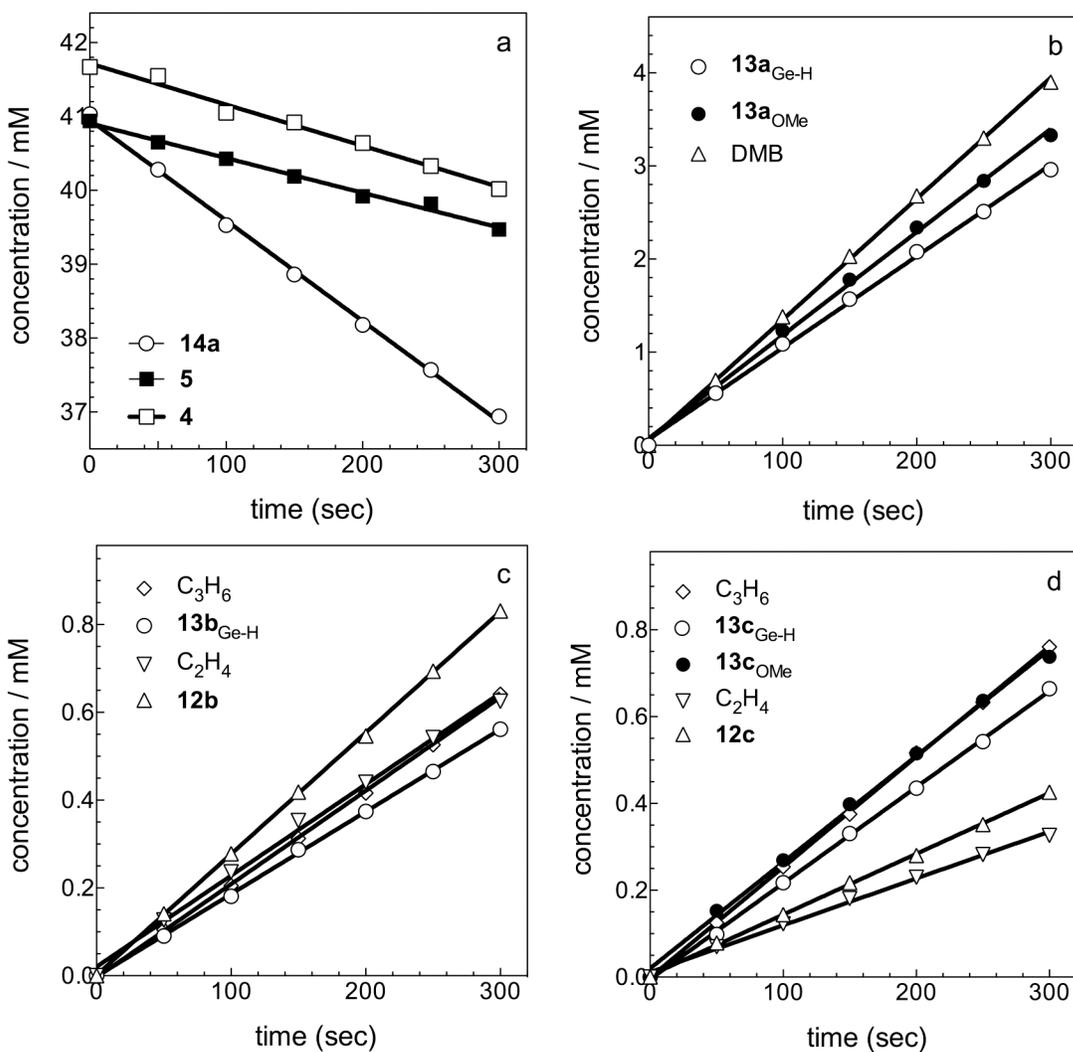


Figure S2. Quantum yield determination for the photolysis of **2** and product concentration vs. time plots, from parallel photolysis of 0.041 M solutions of **2** and **14a** in cyclohexane- d_{12} containing 0.3 M MeOH and hexamethyldisilane (~ 5 mM) as internal integration standard. *Left:* [**2**] and [**14a**] vs. time (slopes: **2**, -0.0061 ± 0.0004 ; **14a**, -0.0128 ± 0.0006). *Right:* [product] vs. time from photolysis of **2** (slopes: C_2H_4 , 0.0025 ± 0.0001 ; **13a**, 0.00359 ± 0.00004 ; C_3H_6 , 0.00118 ± 0.00002 ; **12a**, 0.00126 ± 0.00002). The slopes of the product vs. time plots from photolysis of **14a** (not shown) were: DMB, 0.0130 ± 0.0005 ; **13a** (from OMe), 0.0116 ± 0.0004 . Errors are quoted as $\pm 2\sigma$ from linear least squares analysis of the data.

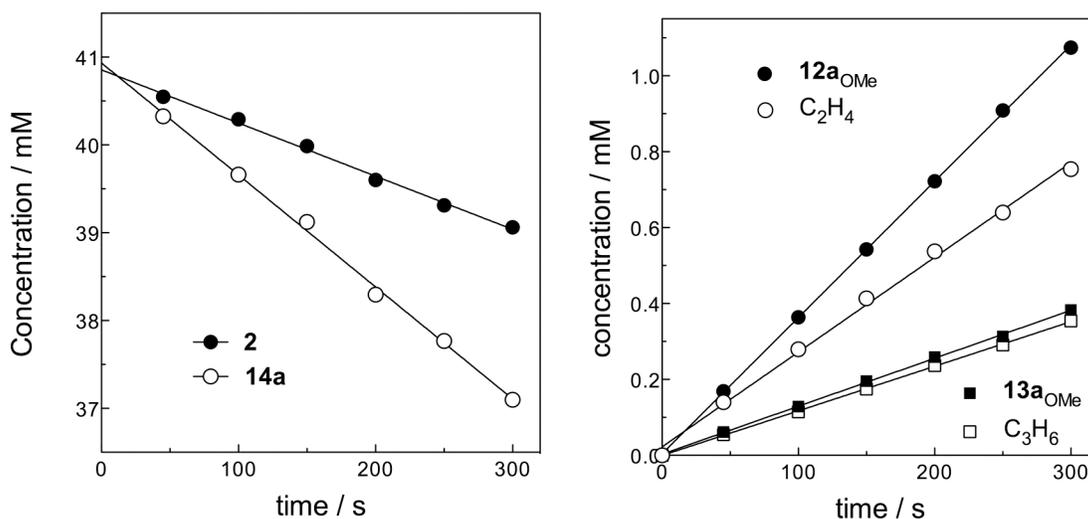


Figure S3. Quantum yield determination for the photolysis of **14c** and product concentration vs. time plots, from parallel photolysis of 0.021 M solutions of **14c** and **14a** in cyclohexane- d_{12} containing 0.3 M MeOH and hexamethyldisilane (~ 5 mM) as internal integration standard. Slopes: **14c**, -0.0082 ± 0.0003 ; DMB from **14c**, 0.0072 ± 0.0001 ; **13c**, 0.0069 ± 0.0001 ; **14a**, -0.0097 ± 0.0004 ; DMB from **14a**, 0.0087 ± 0.0002 ; **13a**, 0.0085 ± 0.0002 . Errors are quoted as $\pm 2\sigma$ from linear least squares analysis of the data.

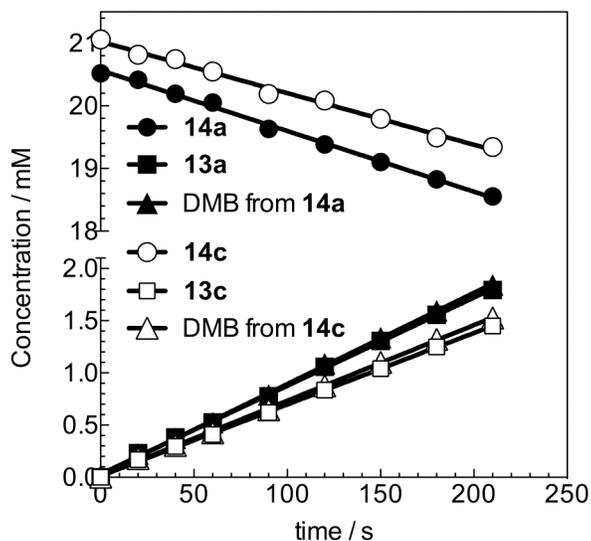


Figure S4. (a) Concentration vs. time plots for **2**, **15a**, **16a**, ethylene, and cyclopropane constructed from ^1H NMR spectra recorded for a 0.04 M solution of **2** in C_6D_{12} containing AcOH (0.05 M) and hexamethyldisilane (1.5 mM) over the 0-5% conversion range in **2**. Slopes: **2**, -0.00438 ± 0.00020 ; **15a**, 0.00312 ± 0.00046 ; C_2H_4 , 0.00206 ± 0.00007 ; **16a**, 0.00100 ± 0.00002 ; C_3H_6 , 0.00110 ± 0.00001 . Errors are quoted as $\pm 2\sigma$ from linear least squares analysis of the data. (b) The ^1H NMR spectrum of the above solution at the highest conversion studied.

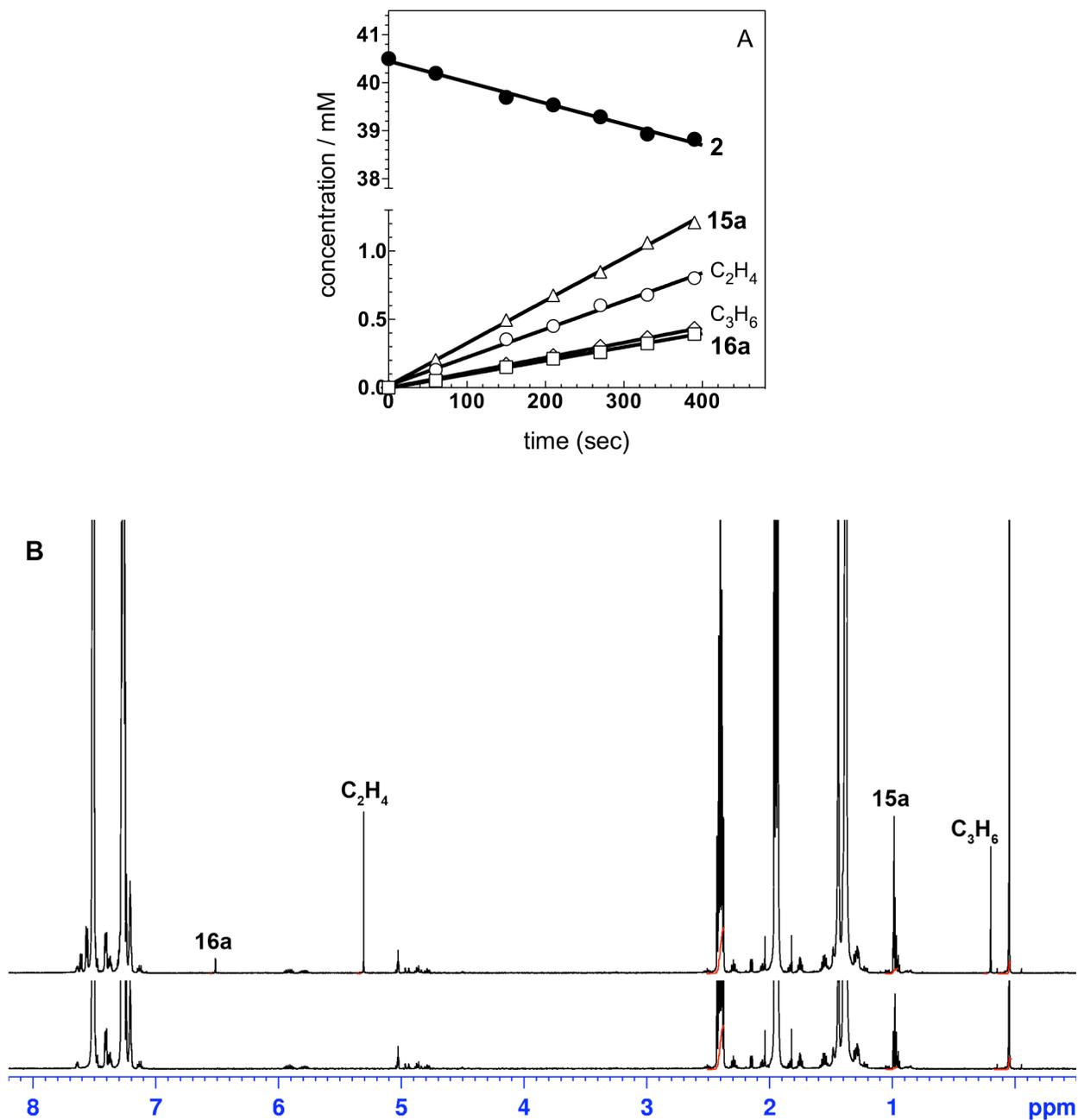


Figure S5. ^1H NMR spectra of a 0.05 M solution **2** in C_6D_{12} containing 0.04 M DMB, before and after photolysis (40 minutes) with 254 nm light.

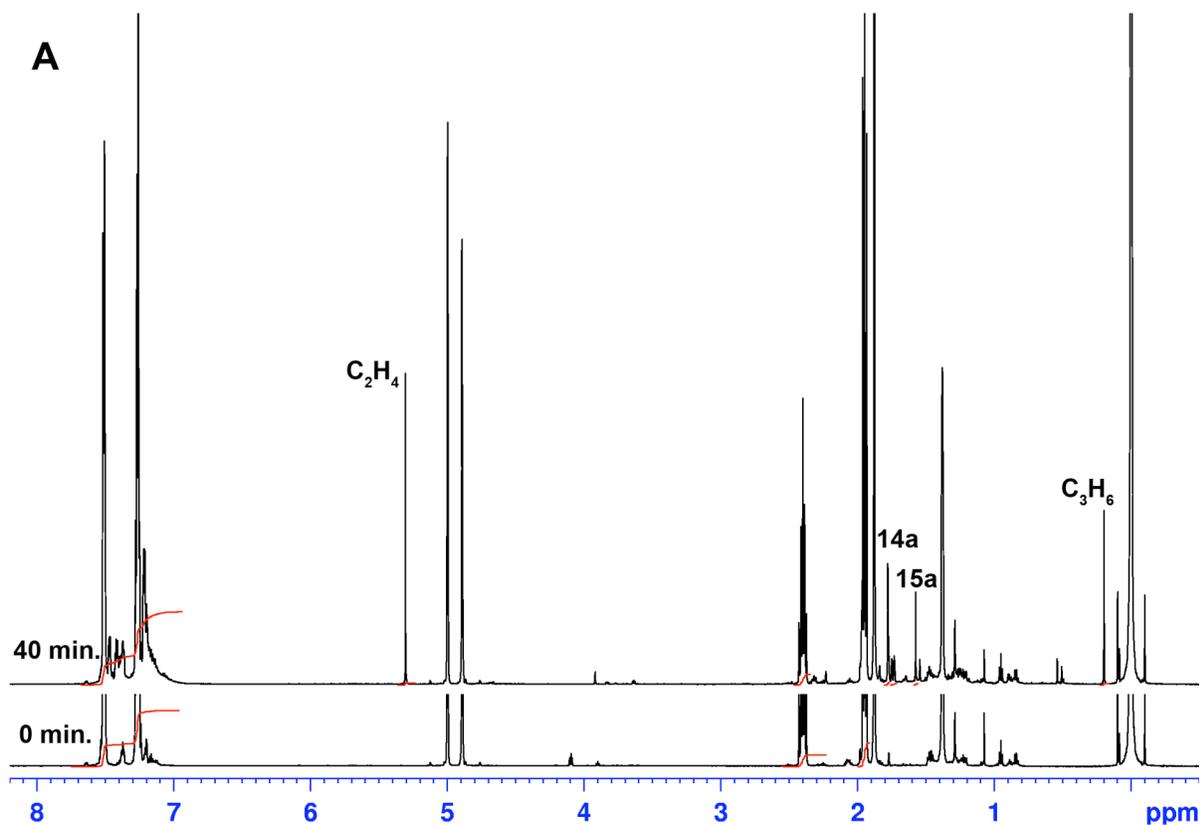


Figure S6. Transient absorption spectra recorded by laser flash photolysis of (a) **4** and (b) **5** in air-saturated hexane at 25 °C, 0 – 0.32 μs (\square) and 85.6 – 86.7 μs (\circ) after the laser pulse. The insets show representative decay traces recorded at 290, 330, and 440 nm.

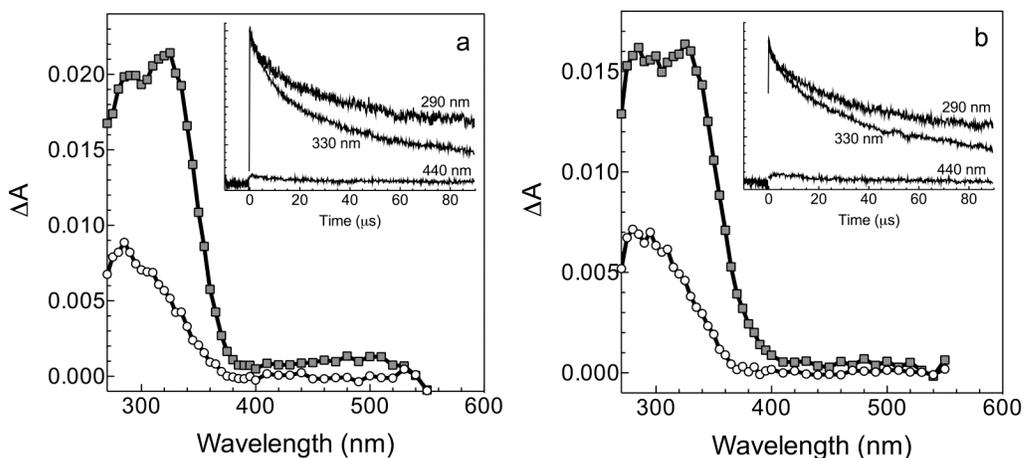


Figure S7. Transient absorption spectra recorded by laser flash photolysis of **4** in air-saturated THF solution at (a) 25 °C and (b) 4 °C, 64 ns – 0.32 μ s (—○—) and 20.03 – 20.29 μ s (—○—) after the laser pulse; also shown are the difference spectra, calculated by subtracting the later from the earlier spectra. The insets show representative decay traces recorded at 325 nm.

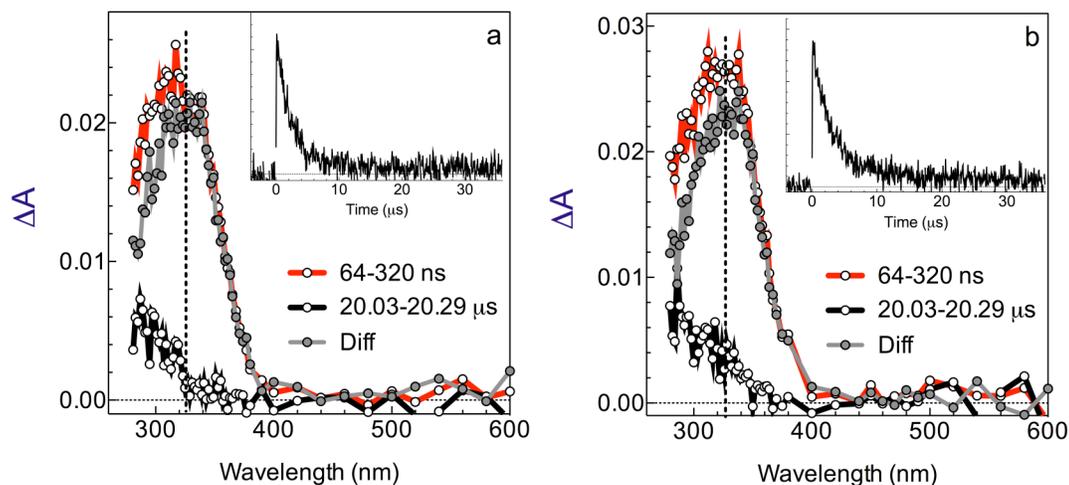


Figure S8. Transient absorption spectra recorded by laser flash photolysis of (a) **14b** and (b) **14c** in deoxygenated MeCN at 25 °C, 0 – 1.25 μ s (\square), 28 – 30 μ s (\circ), and 345 – 348 μ s (Δ) after the laser pulse. The insets show representative decay traces recorded at 300 and 350 nm.

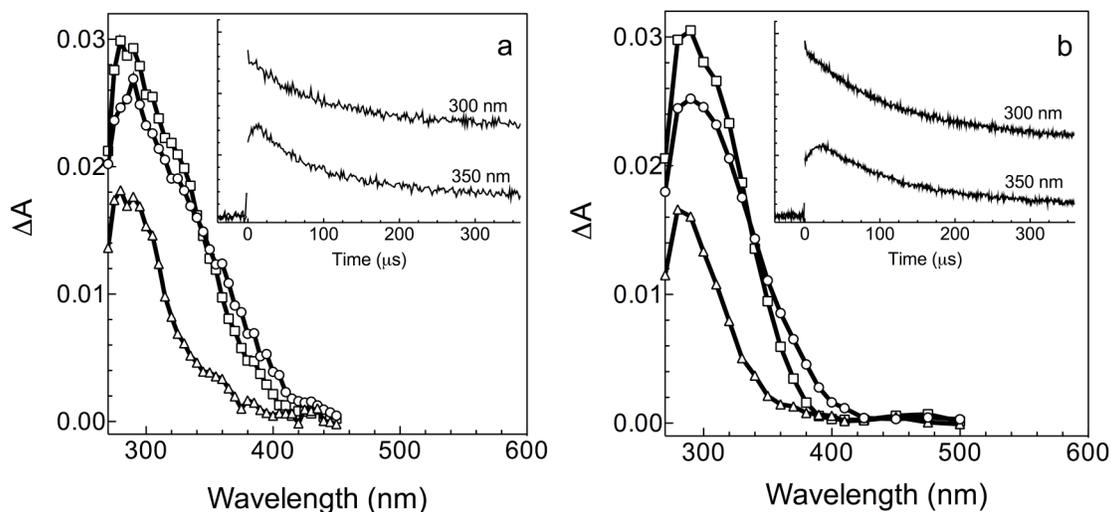


Figure S9. Plots of k_{decay} vs. $[\text{t-BuOH}]$ for quenching of 1,1-diarylgermenes **1** (○), **6** (□), and **7** (Δ) by *tert*-butanol in air-saturated hexane solution at 25 °C. The data for **1** were taken from ref. 1.

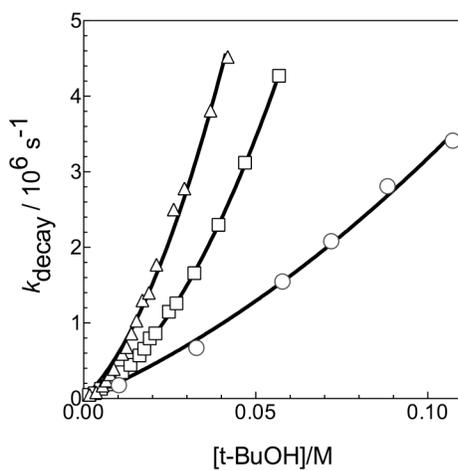


Figure S10. Plots of (a) k_{decay} vs. $[\text{AcOH}]_{\text{bulk}}$ and (b) k_{decay} vs. monomeric AcOH concentration ($[(\text{AcOH})_{\text{mon}}]$), for quenching of 1,1-diarylgermenes **1** (○), **6** (□), and **7** (Δ) by acetic acid in air-saturated hexane solution at 25 °C; $[(\text{AcOH})_{\text{mon}}]$ values were calculated using the monomer-dimer equilibrium constant of Fujii et al ($K_2 = 3200 \pm 500 \text{ M}^{-1}$).⁷ The solid lines in (a) represent the linear least squares fits of the data points below 0.3 mM, from which the rate coefficients listed in Table 1 were obtained. The solid lines in (b) are the linear least squares fits of the complete data sets to eq. 12.

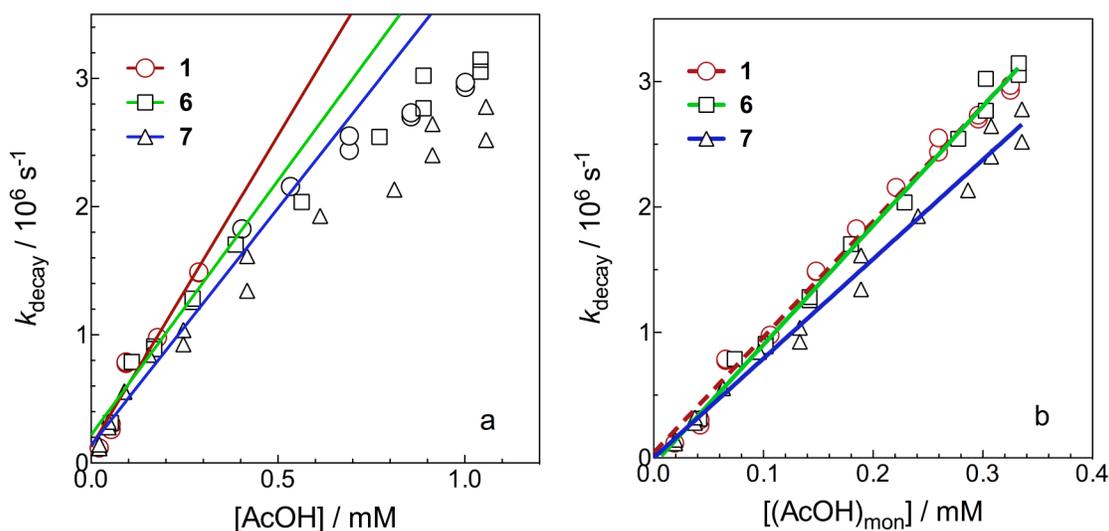


Figure S11. Plots of the pseudo-first order rate constants for germene decay (k_{decay}) for quenching of germenes **6** (○), **7** (□), and **1** (△) versus the concentration of methanol H-bonded dimers, $[(\text{MeOH})_2]$, in air saturated hexane at 25 °C. The solid lines are the best linear least squares fits of the data to equation 16.

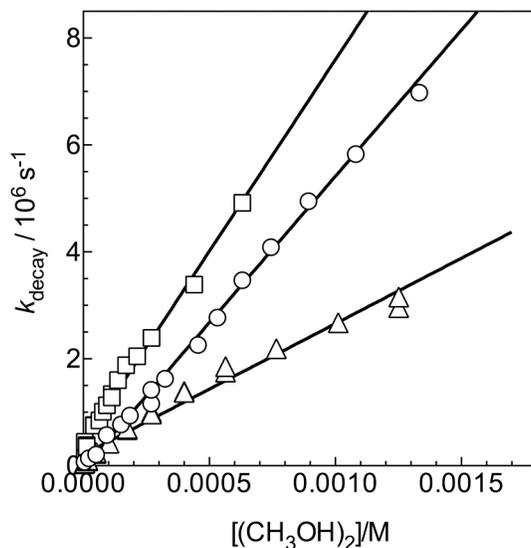


Figure S12. Plots of k_{decay} vs. $[\text{AcOH}]$ for quenching of germenes **1** and **6** by AcOH in MeCN solution over the 25 – 63 °C temperature range.

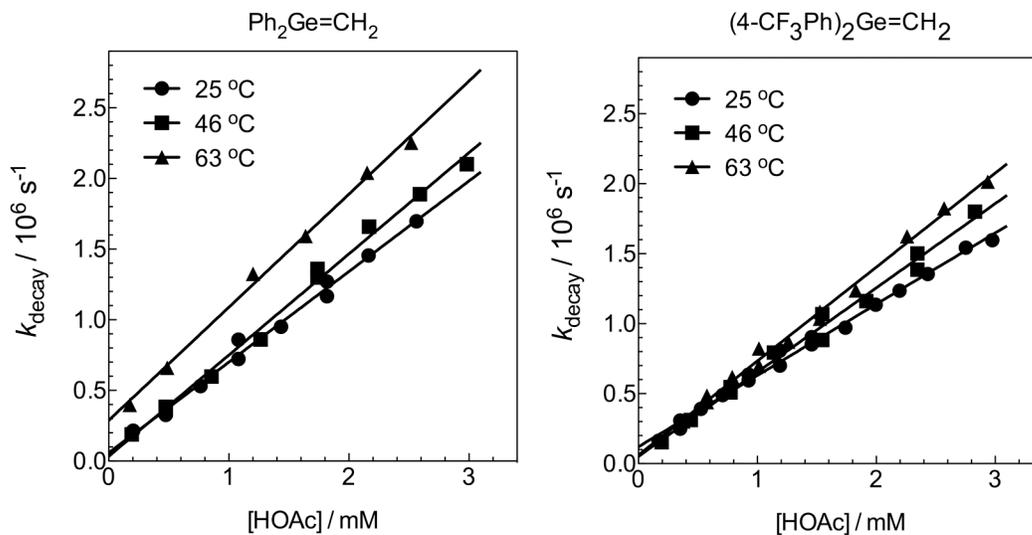


Figure S13. Plots of k_{decay} vs. $[Q]$ for quenching of germenes (a) **6** and (b) **7** by acetone (●) and acetone- d_6 (○) in air-saturated hexane solution at 25°C.

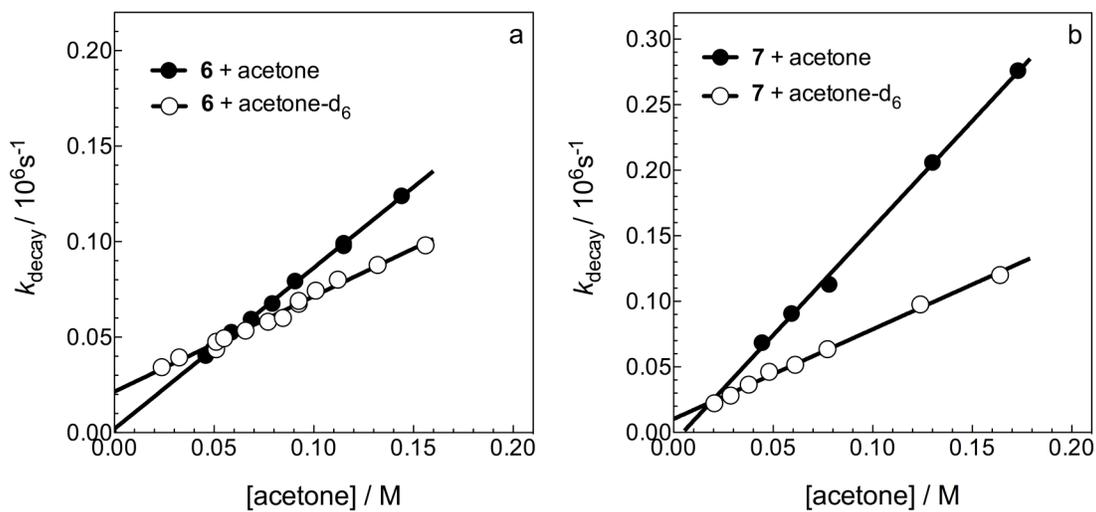
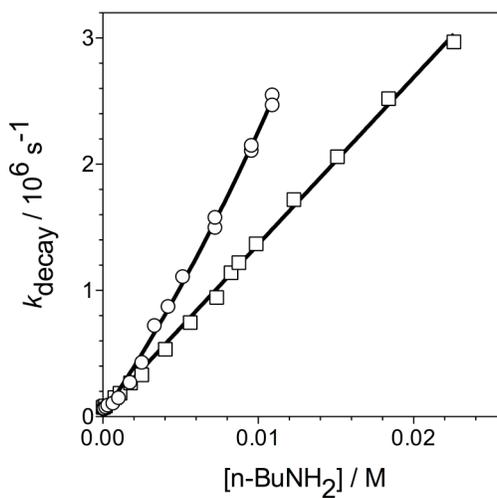


Figure S14. Plots of k_{decay} vs. $[Q]$ for quenching of germenes **6** (□) and **7** (○) by $n\text{-BuNH}_2$ in air-saturated hexane solution at 25°C.



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