Supporting Information for

Fast Kinetic Studies of the Reactivities of Transient Germylenes in Methanol and Tetrahydrofuran Solution

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Synthesis and Characterization of Compounds

^{1}H NMR spectra were recorded on Bruker AV200 or AV600 NMR spectrometers in $CDCl_3$, THF-d_8, or cyclohexane-d_{12} solution and are reported in parts per million (δ) downfield from tetramethylsilane; spectra were calibrated using the residual solvent-proton resonances as the internal standard. 150 MHz ^{13}C NMR spectra were recorded on the Bruker AV600 spectrometer and were calibrated using the solvent signals. Infrared spectra were recorded on a BioRad FTS-40 FTIR spectrophotometer and are reported in wavenumbers (cm^{-1}). Elemental analyses were performed 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. Column chromatography was carried out using acid-washed 230-400 mesh silica gel (Silicycle).

GC/MS analyses were carried out on a Varian Saturn 2200 GC/MS/MS system equipped with a VF-5ms capillary column (30 m × 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.), using (70 eV) electron impact ionization; *m/z* values marked with an asterisk indicate ions containing ^{74}Ge. High resolution exact masses were determined on the latter instrument using a mass of 12.000000 for carbon-12.

Sodium (Aldrich, 99%), magnesium (EM Science, >99%), 2,3-dimethyl-1,3-butadiene (Aldrich), methanol (Caledon, HPLC grade or J. T. Baker, absolute), glacial acetic acid (Caledon), methanol-OD (Aldrich), and acetic acid-OD (Aldrich) were used as received from the suppliers. Chloroform-d, cyclohexane-d_{12}, and tetrahydrofuran-d_8 were used as received from Cambridge Isotope Labs.

Diethyl ether (Caledon Reagent), THF (Caledon HPLC grade), and hexanes (EMD, OmniSolv) were dried by passage through activated alumina (250 mesh, neutral) under nitrogen using a Solv-Tec solvent purification system (Solv-Tec, Inc.). Acetonitrile (Caledon, HPLC grade) was refluxed over CaH_2 and distilled. Germanium tetrachloride (Gelest, Inc. or Teck-Cominco Metals, Ltd.) was

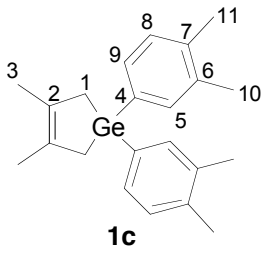
used as received from the suppliers. $GeCl_2$-dioxane,[1] 1,1-dichloro-3,4-dimethyl germacyclopent-3-ene,[2] 1,1-dichloro-3-methylgermacyclopent-3-ene,[2] 3,4-dimethyl-1,1-diarylgermacyclopent-3-enes (**1a,b,d,e**),[3] and 1,1-dimethyl-3-phenylgermacyclopent-3-ene (**3**)[4] were prepared and purified as previously reported. All synthetic manipulations were carried out in flame-dried glassware under an atmosphere of dry argon or nitrogen.

1-Bromo-3,4-dimethylbenzene was prepared by a modification of the method of Doyle and coworkers.[5] In a flame-dried 1 L round bottom flask, anhydrous acetonitrile (500 mL) was rapidly stirred under nitrogen and cooled to 5°C in an ice bath. *tert*-Butyl nitrite (41.78 g, 405 mmol) and $CuBr_2$ (72.04 g, 324 mmol) were added in one portion with stirring and the mixture was then stirred for 2 hrs at 5°C. To the resulting dark green mixture 3,4-dimethylaniline (32.45 g, 270 mmol) in dry acetonitrile (200 mL) was added dropwise over 2 h at 5 °C, after which it was stirred overnight at room temperature while a steady stream of gas was evolved. Hydrochloric acid (20%; 1.0 L) was added to the reaction mixture, which was then extracted with diethyl ether (4 x 500 mL). The organic extracts were washed with 10% aqueous sodium bicarbonate (500 mL) and water (500 mL), dried over anhydrous $MgSO_4$, and then evaporated to yield a dark red oil (60 g). TLC (silica, 1:2 CH_2Cl_2-hexanes) showed the presence of two mobile fractions (R_f = 0.67 and 0.56). Flash column chromatography (silica gel; 1:2 CH_2Cl_2-hexanes) allowed isolation of the two components, with the R_f = 0.67 compound identified as the target product by comparison (GC/MS and TLC) to an authentic sample (Sigma-Aldrich; 70%). The fractions were concentrated to yield a cloudy white liquid (39.57 g), which was distilled twice (b.p. 68 °C, 0.15 mmHg) to obtain the product as a colorless liquid (16.27 g, 33%). ^{1}H NMR: δ 2.20 (s, 3H), 2.23 (s, 3H), 6.99 (d, 1H, J = 8.4 Hz), 7.21 (d, 1H, J = 8.4 Hz), 7.27 (s, 1H). ^{13}C NMR: δ 19.38, 19.72, 119.29, 128.81, 131.28, 132.41, 135.58, 138.92.

1,1-bis(3,4-dimethylphenyl)-3,4-dimethylgermacyclopent-3-ene (**1c**). In a 250 mL flame-dried two-necked round bottom flask equipped with an addition funnel, stir bar and reflux condenser, freshly

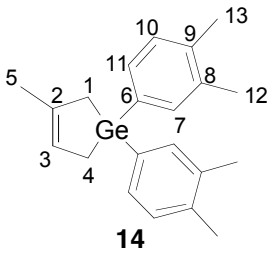
ground magnesium turnings (0.96 g, 39.59 mmol) and anhydrous THF (50 mL) were allowed to stir with a few drops of 1,2-dibromoethane. Once the initial bubbling had subsided, a solution of 1-bromo-3,4-dimethylbenzene (6.66 g, 35.99 mmol) in anhydrous THF (40 mL) was added dropwise over four hours. The addition funnel was replaced with a stopper and the reaction refluxed with rapid stirring overnight. The resulting dark brown solution of 3,4-dimethylphenyl magnesium bromide was cooled in an ice bath. A solution of 1,1-dichloro-3,4-dimethyl-2,5-dihydro-1H-germole (3.25 g, 14.39 mmol) in anhydrous THF (40 mL) was then added dropwise over one hour, and the resulting solution was stirred at room temperature overnight. The reaction mixture was washed with water (2 × 100 mL) and aqueous NH_4Cl (1 M, 1 × 80 mL), extracted with ether (3 × 100 mL), dried over anhydrous $MgSO_4$, and evaporated to yield a pale brown oil (8.25 g). Purification by column chromatography (silica, 1:2 CH_2Cl_2-hexane) afforded a colorless oil, which slowly crystallized to form colorless crystals (1.4 g, 3.8 mmol, 26%). The material was further purified by several slow recrystallizations from hexanes, and identified as 1,1-bis(3,4-dimethylphenyl)-3,4-dimethyl-2,5-dihydro-1H-germole (**1c**; m.p. 62.0-63.0 ^{o}C) on the basis of the following spectroscopic and analytical data.

^{1}H NMR, δ = 1.77 (s, 6H, H^{3}), 1.96 (s, 4H, H^{1}), 2.25 (s, 6H, H^{11}), 2.26 (s, 6H, H^{10}), 7.13 (d, 2H, J = 7.2 Hz, H^{8}), 7.25 (d, 2H, J = 7.2 Hz, H^{9}), 7.28 (s, 2H, H^{5}). ^{13}C NMR, δ = 19.58 (C^{3}), 19.84 ($C^{10 \text{ or } 11}$), 19.85 ($C^{10 \text{ or } 11}$), 25.79 (C^{1}), 129.61 (C^{8}), 130.90 (C^{2}), 131.96 (C^{9}), 135.47 ($C^{4 \text{ and } 5}$ by 2D NMR), 136.50 (C^{7}), 137.58 (C^{6}). MS, m/z (intensity): 366.1* (40), 284.1* (90), 209.1* (100), 179.0 (75), 145.1 (30), 91.1 (40), 67.1 (70). HRMS: $C_{22}H_{28}{}^{74}Ge$: calc.: 366.1407, found: 366.1386. IR, cm^{-1} (intensity): 3092 (w), 3048 (m), 2998 (s), 2967 (s), 2915 (s), 2584 (s), 2780 (w), 2724 (w), 1890 (w), 1762 (w), 1447 (s), 1098 (s), 810 (s). Anal. calc. for $C_{22}H_{28}Ge$: C 72.37, H 7.73, found: C, 72.43; H, 7.90.



1c

1,1-Bis(3,4-dimethylphenyl)-3-methylgermacyclopent-3-ene (**14**) was prepared in a manner analogous to that of **1c**, except that 1,1-dichloro-3-methyl-2,5-dihydro-1H-germole (0.45, 2.1 mmol) was used in place of 1,1-dichloro-3,4-dimethyl-2,5-dihydro-1H-germole. It was isolated as a colorless oil (0.39 g, 1.1 mmol, 52%) from the crude reaction mixture by silica gel column chromatography (1:2 CH_2Cl_2-hexanes) and identified as 1,1-bis(3,4-dimethylphenyl)-3-methyl-2,5-dihydro-1H-germole (**14**) based on the following spectroscopic data: ^{1}H NMR, δ = 1.84 (br s, 5H, H^4 and H^5), 1.94 (s, 2H, H^1), 2.25 (s, 6H, H^{12} or H^{13}), 2.26 (s, 6H, H^{12} or H^{13}), 5.70 (s, H, H^3), 7.13 (d, 2H, J = 7.2 Hz, H^{10}), 7.25 (d, 2H, J = 7.2 Hz, H^{11}), 7.28 (s, 2H, H^{11}).^{13}C NMR, δ = 19.33 (C^1), 19.83 (C^{12} or C^{13}), 19.88 (C^{12} or C^{13}), 22.68 (C^5), 22.89 (C^4), 125.41 (C^3), 129.64 (C^{10}), 131.88 (C^{11}), 135.40 (C^7), 135.43 (C^8), 136.55 (C^9), 137.47 (C^6), 140.28 (C^2).MS, m/z (intensity): 352.1* (8), 284.1* (12), 210.1 (100), 195.1 (53), 179.1 (19). HRMS: calc. for $C_{21}H_{26}{}^{74}Ge$, 352.1246; found: 352.1234. IR, cm^{-1} (intensity): 2998 (br, s), 2917 (br, s), 1637 (w), 1494 (m), 1447 (s), 1377 (m), 1147 (w), 1098 (s), 810 (m), 720 (m).



14

Steady-State Photolysis Experiments

*(a) Photolysis of 1,1-dimethyl-3-phenylgermacyclopent-3-ene (**3**) in THF-d_8 containing AcOH.*

A solution of **3** (0.025 M) in THF-d_8 containing AcOH (0.04 M) and hexamethyldisilane (0.005 M) as internal integration standard was placed in a quartz NMR tube, deoxygenated with a stream of dry argon, sealed with a rubber septum, and irradiated with 6 RPR-2537 lamps in a Rayonet photochemical reactor. The course of the photolysis was monitored as a function of time by ^{1}H NMR spectroscopy up to ca. 40% conversion of **3**. Representative NMR spectra are shown in Fig. S1. Only two products were formed, which were identified as 2-phenyl-1,3-butadiene (**PBD**; δ 7.26-7.33 (m, 6H), 6.63 (dd, 1H; J = 10.8, 17.3 Hz), 5.13-5.18 (m, 4H)) and acetoxydimethylgermane (**6**; δ 5.596 (sept, 1H, J = 2.4 Hz), 1.92 (s, 3H), 0.58 (d, 6H, ^3J = 2.4 Hz).

Product yields were determined relative to consumed **3** from the slopes of concentration vs. time plots for **3**, **PBD**, and **6** (see Fig. S2), constructed by integration of the spectra.

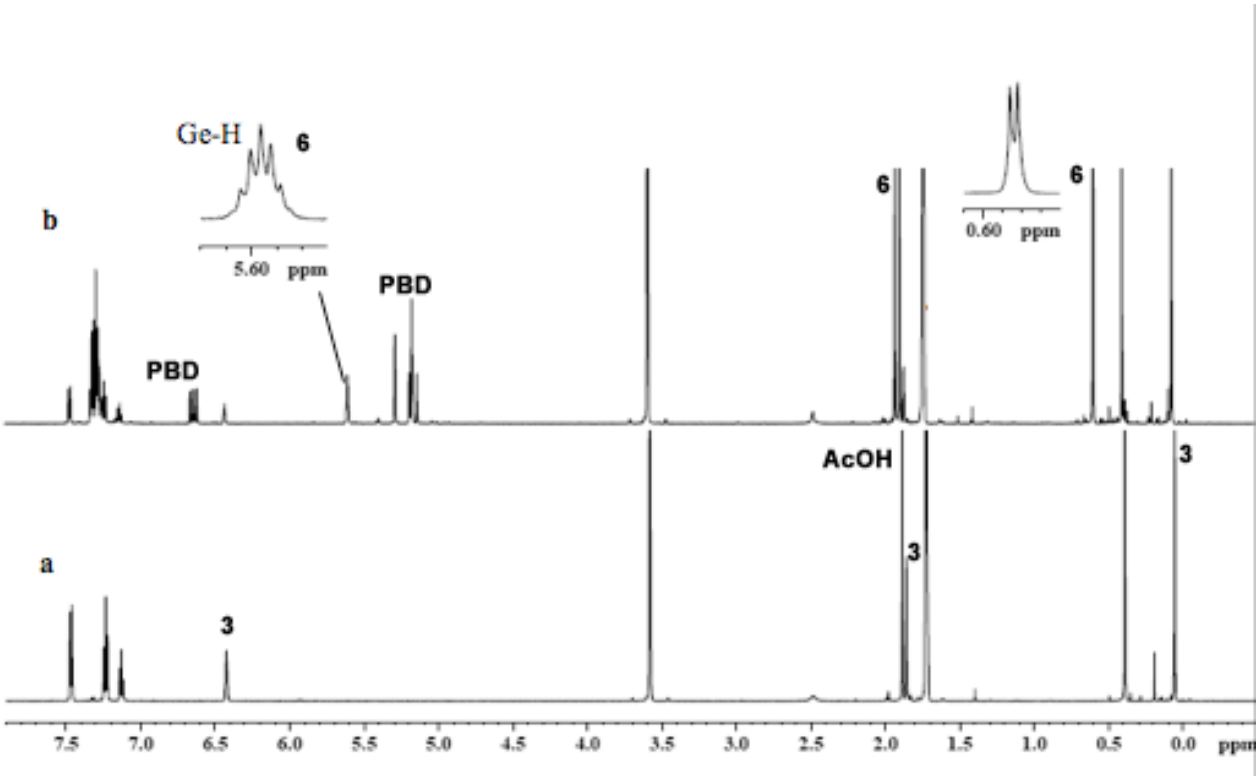


Figure S1. 600 MHz ^{1}H NMR spectra of the crude reaction mixture from photolysis of **3** (0.025 M) in deoxygenated THF-d_8 containing AcOH (0.04 M) and hexamethyldisilane as integration standard: (**a**) before photolysis and (**b**) after ca. 40 % conversion of **3**.

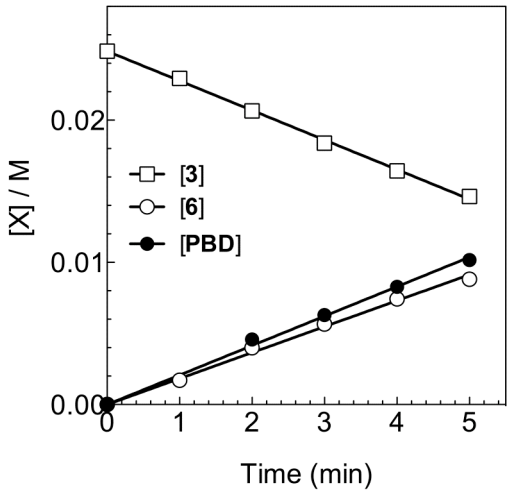


Figure S2. Concentration vs. time plots for **3** (□), **PBD** (●), and **6** (○) from the photolysis of **3** (0.025 M) in deoxygenated THF-d_8 containing AcOH (0.04 M). Slopes: **3**, -0.00208 ± 0.00004; **PBD**, +0.00207 ± 0.00003; **6**, +0.00183 ± 0.00003.

*(b) Photolysis of 1,1-dimethyl-3-phenylgermacyclopent-3-ene (**3**) in THF-d_8 containing $MeSO_3H$.*

A solution of **3** (0.034 M) in THF-d_8 containing $MeSO_3H$ (0.09 M) and hexamethyldisilane (0.005 M) as internal integration standard was placed in a quartz NMR tube, deoxygenated with a

stream of dry argon, sealed with a rubber septum, and irradiated with 6 RPR-2537 lamps in a Rayonet photochemical reactor. The course of the photolysis was monitored as a function of time by ^{1}H NMR spectroscopy up to ca. 60% conversion of **3**; representative NMR spectra are shown in Fig. S3. The product exhibiting multiplets at δ 5.90 (sept (J = 2.0 Hz), 1H) and 0.76 (d (J = 2.0 Hz), 6H) is tentatively identified as $Me_2Ge(H)OSO_2H$ (**7**). Product yields were determined relative to consumed **3** from the slopes of concentration vs. time plots for **3**, **PBD**, and **7** (see Fig. S4), constructed by integration of the spectra.

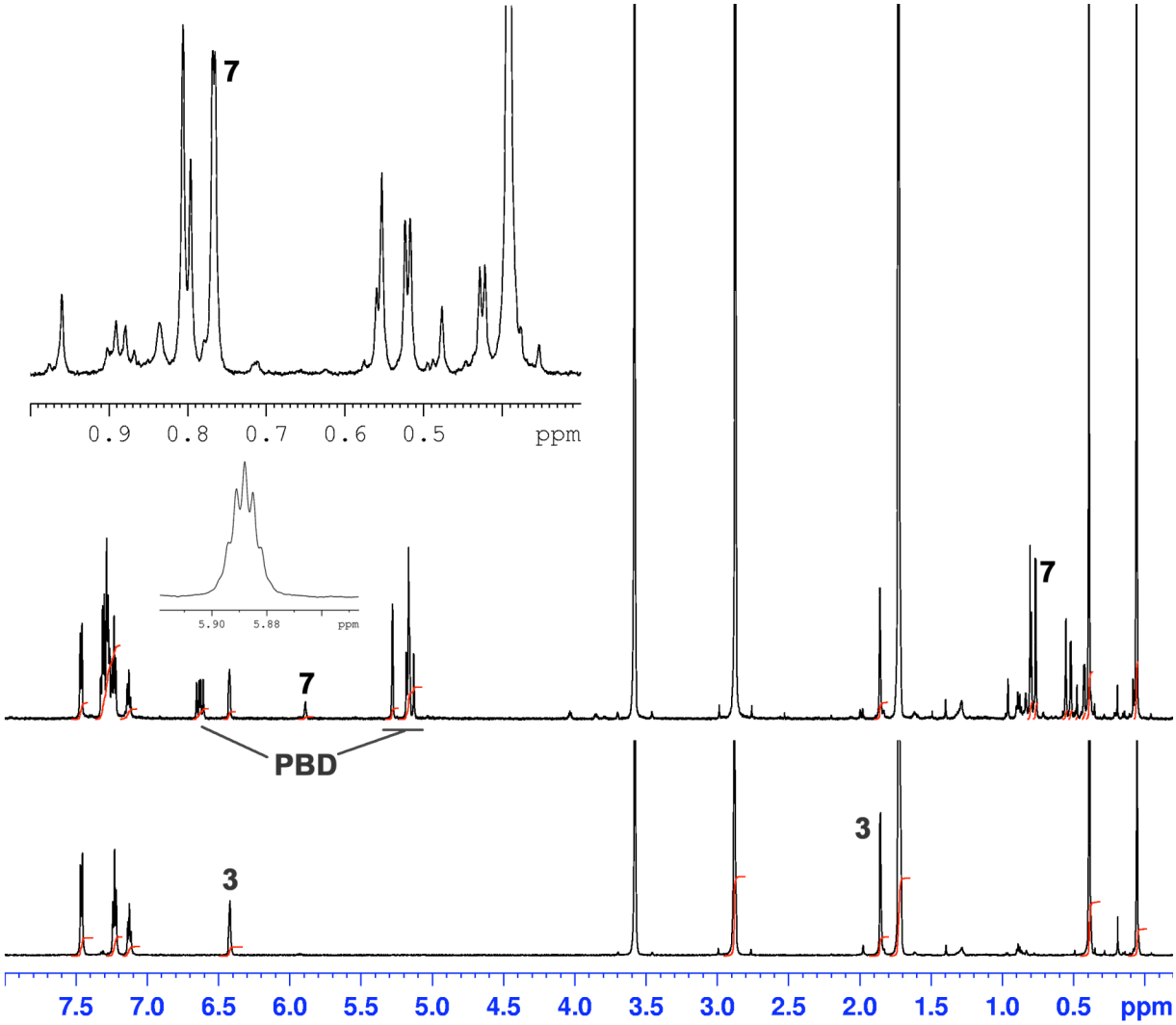


Figure S3. 600 MHz ^{1}H NMR spectra of the crude reaction mixture from photolysis of **3** (0.034 M) in deoxygenated THF-d_8 containing $MeSO_3H$ (0.09 M) and hexamethyldisilane as integration standard: (**a**) before photolysis and (**b**) after ca. 60 % conversion of **3** (10 minutes photolysis).

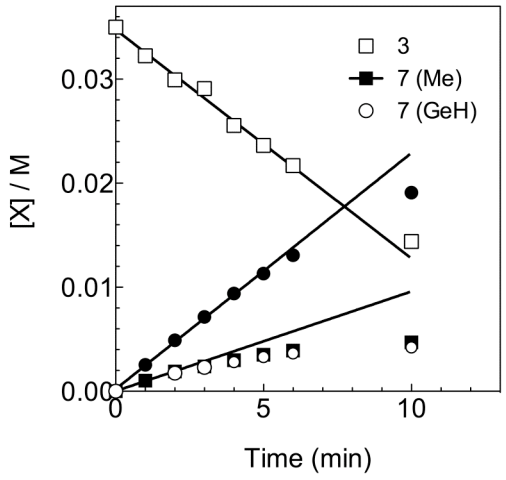
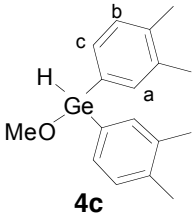


Figure S4. Concentration vs. time plots for **3** (□), **PBD** (●), and **7** (○, ■) from the photolysis of **3** (0.034 M) in deoxygenated THF-d_8 containing $MeSO_3H$ (0.09 M). Slopes: **3**, -0.00220 ± 0.00010; **PBD**, +0.00227 ± 0.00005; **7**, +0.00096 ± 0.00003.

(c) Photolysis of 1,1-bis(3,4-dimethylphenyl)-3,4-dimethylgermacyclopent-3-ene (**1c**) *in cyclohexane-d_{12} containing MeOH. Determination of the quantum yield of germylene formation.*

Solutions of **1a** and **1c** (0.02 M) in C_6D_{12} containing MeOH (0.2 M) and a trace of Si_2Me_6 as an internal integration standard were irradiated together in a merry-go-round, monitoring the solutions by ^{1}H NMR spectroscopy at 30 second intervals to ca. 8% conversion. In each solution, DMB and the corresponding methoxygermane (**4a**,**c**) were the only detectable products.



4c

Identification of **4c** was made on the basis of comparisons of its ^{1}H NMR spectra to that of **4a**.[6] The quantum yield for formation of **4c** from **1c** was determined to be $\Phi = 0.35 \pm 0.08$, from the slopes of concentration vs. time plots (Fig. S5) constructed from the NMR data, relative to that for formation of **4a** from **1a** ($\Phi = 0.55 \pm 0.07$).[6] ^{1}H NMR **4c** (C_6D_{12}): δ = 2.21 (s, 6H, ArMe), 2.22 (s, 6H, ArMe), 3.49 (s, 3H, OMe), 6.02 (s, H, GeH), 7.06 (d, 2H, J = 7.2 Hz, H^b), 7.23 (d, 2H, J = 7.2 Hz, H^c), 7.29 (s, 2H, H^a).

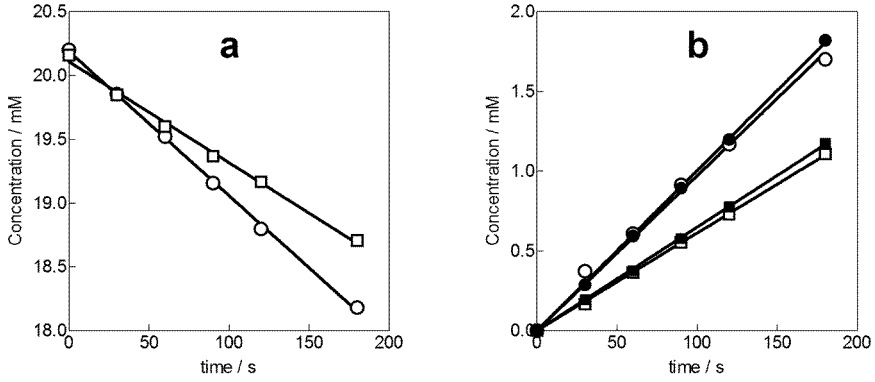
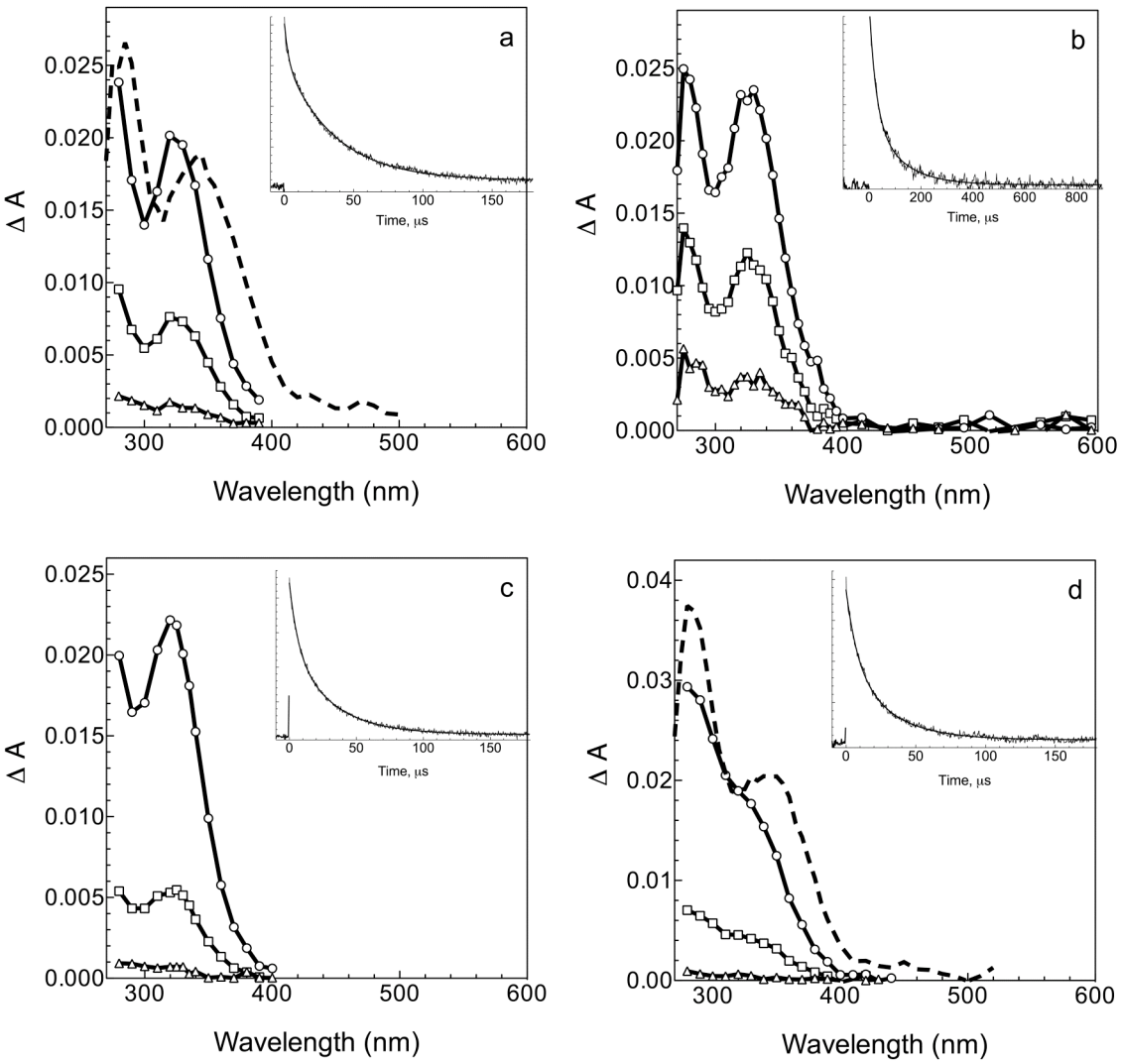


Figure S5. Concentration vs. time plots from the parallel photolyses of solutions of **1a** and **1c** (0.02 M) in C_6D_{12} containing MeOH (0.2 M); (a) **1a** [○] and **1c** [□]; (b) **4a** [○] and DMB [●], **4c** [■] and DMB [□]. Slopes: **1a**, -0.01131 ± 0.00017; **4a**, +0.00971 ± 0.00019; DMB (from **1a**), +0.01004 ± 0.00004; **1c**, -0.01131 ± 0.00017; **4c**, +0.00612 ± 0.00004; DMB (from **1c**), +0.00649 ± 0.00003.

(d) Photolysis of 1,1-bis(3,4-dimethylphenyl)-3,4-dimethylgermacyclopent-3-ene (**1c**) *in hexanes containing isoprene.* Additional confirmation of germylene extrusion from **1c** was obtained by photolysis of **1c** (2 mM) in deoxygenated hexanes in the presence of isoprene (2 mM). A single product was detected by GC/MS which was identified as **14** based on co-injection with the authentic sample.

Laser Flash Photolysis Experiments

Figure S6. Transient absorption spectra from laser flash photolysis of (a) **1b**, (b) **1c**, (c) **1d**, and (d) **1e**, recorded 0-0.64 μs (○), 27.5-28.5 μs (□), and 107.5-108.5 μs after the laser pulse in deoxygenated MeOH solution at 25 ^{o}C; the insets show transient decay profiles recorded at 320 nm. The dotted lines in (a) and (d) show spectra recorded by laser photolysis of **1b** and **1e** in hexane containing ca. 10 mM MeOH; the corresponding spectra from **1c** and **1d** were not recorded.



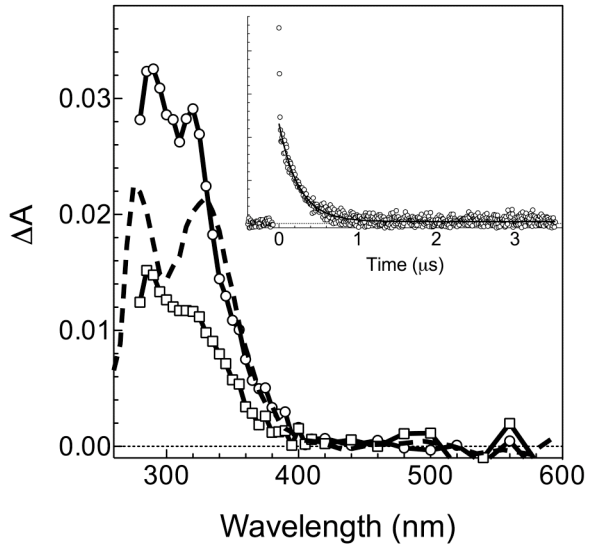


Figure S7. Transient absorption spectra from laser flash photolysis of **1c**, recorded 0-26 ns (○) and 150-200 ns (□) after the laser pulse in deoxygenated MeOH solution containing 0.9 mM $MeSO_3H$; the inset shows a transient decay profile recorded at 320 nm. The dotted line is the spectrum of **8c** in the absence of added acid.

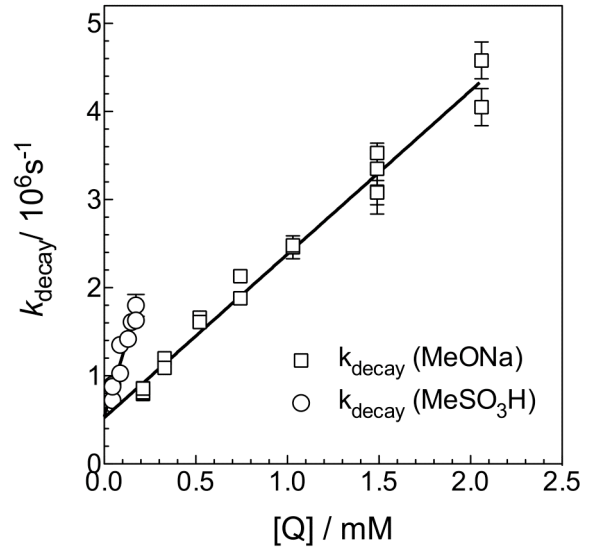


Figure S8. Plots of k_{decay} vs. [Q] for quenching of the $GeMe_2$-MeOH complex (**9**) by $MeSO_3H$ and MeONa in MeOH at 25 °C. The solid lines are the linear least squares fits of the data to eq. 8 in the paper, corresponding to slopes of k_{MeSO3H} = (7.7 ± 0.9) x 10^9 $M^{-1}s^{-1}$ and k_{MeONa} = (1.8 ± 0.2) x 10^9 $M^{-1}s^{-1}$.

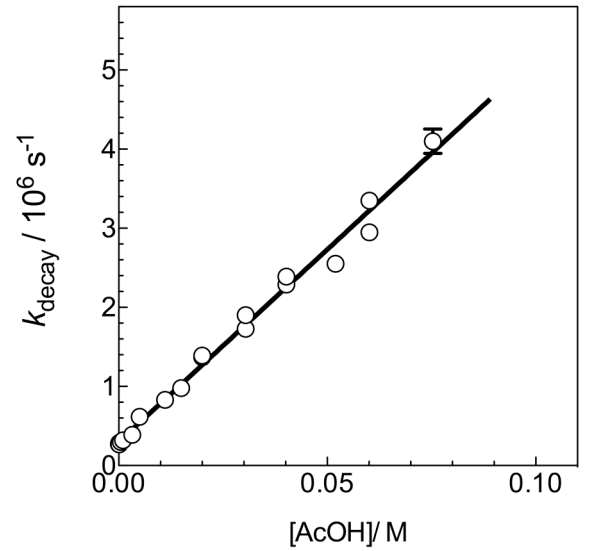


Figure S9. Plot of k_{decay} vs. [AcOH] for quenching of the $GeMe_2$-MeOH complex (**9**) by AcOH in MeOH at 25 °C. The solid line is the linear least squares fit of the data to eq. 8 in the paper, corresponding to a slope of k_{AcOH} = (4.9 ± 0.3) x 10^7 $M^{-1}s^{-1}$.

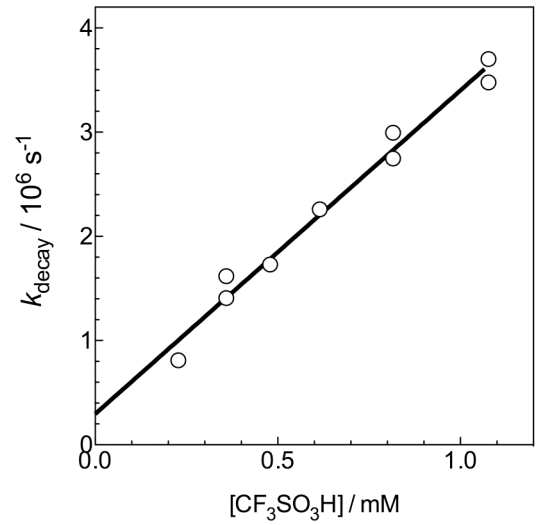


Figure S10. Plot of k_{decay} vs. [CF_3SO_3H] for quenching of the $GePh_2$-MeOH complex (**8a**) by trifluoromethanesulfonic acid in MeOH at 25 °C. The solid line is the least squares fit of the data to eq. 8 in the paper, corresponding to a slope of $k_{CF_3SO_3H}$ = (3.1 ± 0.3) x 10^9 $M^{-1}s^{-1}$.

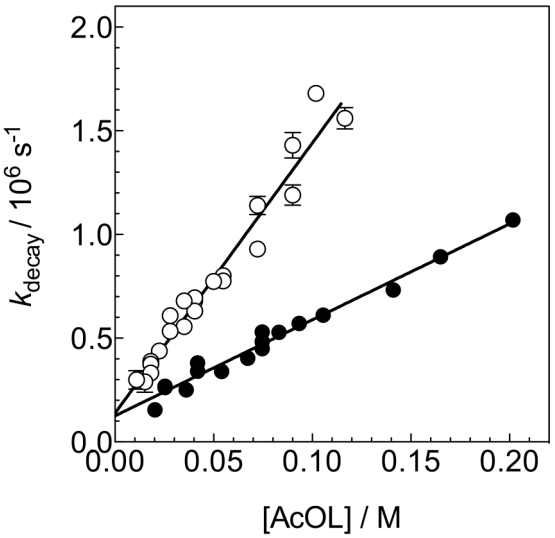


Figure S11. Plots of k_{decay} vs. [AcOL] for quenching of the $GeMe_2$-THF complex (**13**) by AcOH (○) and AcOD (●) in THF at 25 °C. The solid lines are the linear least squares fits of the data to eq. 8 in the paper, corresponding to slopes of k_{AcOH} = (1.3 ± 0.1) x 10^7 $M^{-1}s^{-1}$ and k_{AcOD} = (4.6 ± 0.4) x 10^6 $M^{-1}s^{-1}$.

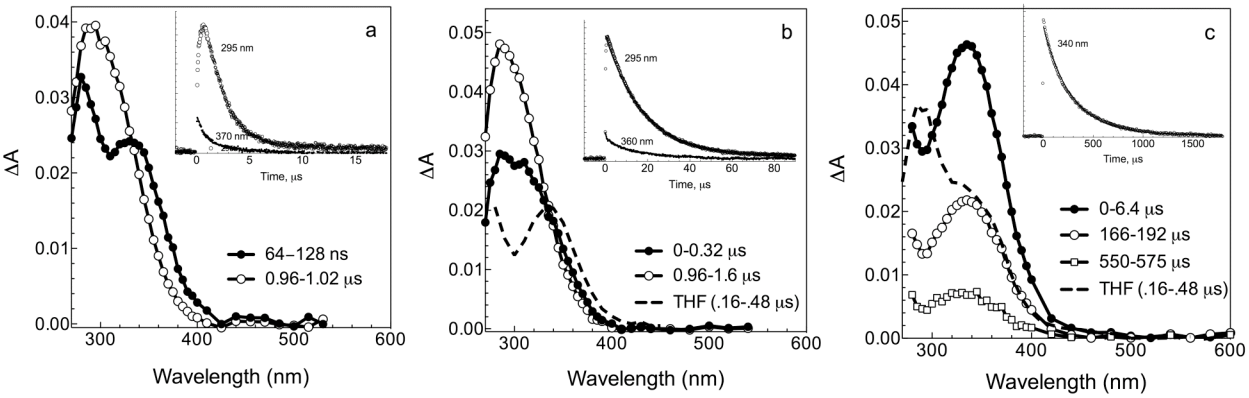


Figure S12. Transient absorption spectra from laser photolysis of (a) **1b**, (b) **1d**, and (c) **1e** in deoxygenated THF solution containing 7.5-8.5 mM MeONa / 0.4 M MeOH at 25 °C; the insets show transient decay profiles recorded at 295 nm (a,b) and 340 nm (c). The time windows over which each of the spectra were recorded are indicated. The spectra shown in dashed lines in (b) and (c) are those of the $GeAr_2$-THF complexes in the absence of added MeONa/MeOH.

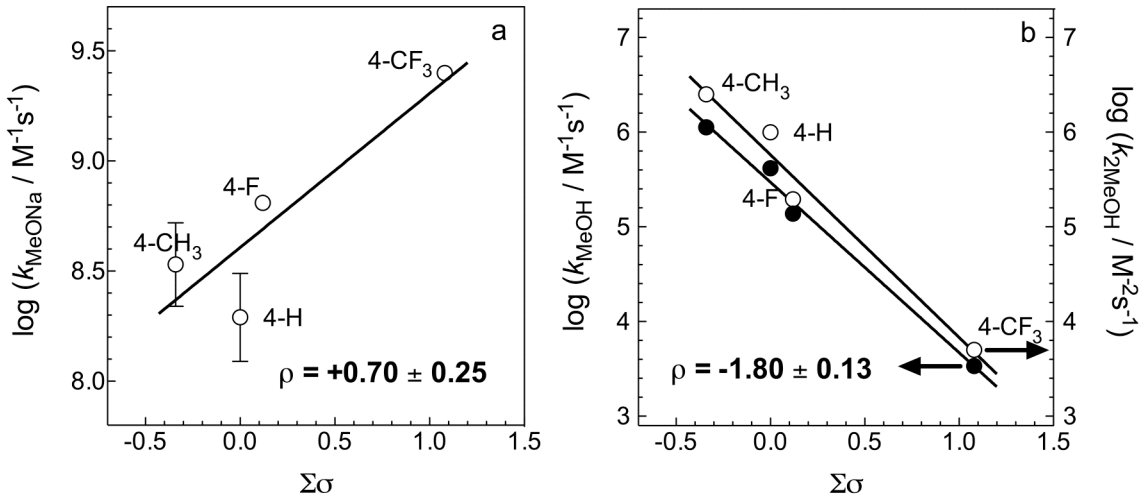


Figure S13. Hammett plots for (a) formation and (b) protonation of diarylgermyl anions in THF containing 7.5-8.5 mM MeONa + 0.35-0.42 M MeOH. The k_{MeONa}-values were estimated from the pseudo-first order rate constants for growth of the anion absorptions ($k_{MeONa} = k_{growth}/[MeONa]$), while the k_{MeOH} values were estimated from the pseudo-first order rate constants for their decay ($k_{MeOH} = k_{decay}/[MeOH]$); the k_{2MeOH} values plotted in (b) are the slopes of (linear) plots of k_{decay} vs. $[MeOH]^2$. The solid lines are the fits of the data to the Hammett equation ($\log k_X = \log k_H + \rho\Sigma\sigma$).

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