Supplementary Information

Kinetics and Mechanisms of the Reactions of Diaryl- and Dialkylgermylenes with Alcohols and Ethers in Solution.

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Figure S1. Raw transient decay profiles at 500 nm, from laser flash photolysis of **1a** in hexane in the absence (—) and presence (—) of 1 mM THF, the latter showing the rapid decay of free $GePh_2$ (τ ~ 145 ns) superimposed on the underlying absorption due to Ge_2Ph_4 in the presence of the ether. The heavy solid line is the transient absorption profile recorded at 440 nm in the presence of 1 mM THF, multiplied by a factor of 0.15.

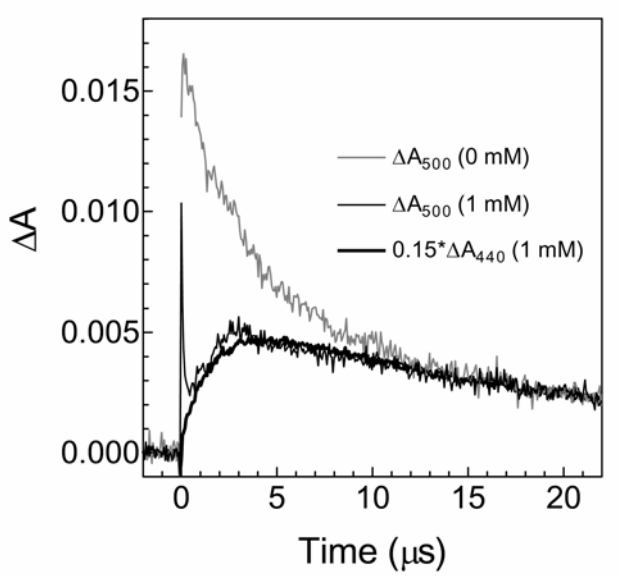

Figure S2. Additional kinetic data on the complexation of $GePh_2$ and THF in hexane at 25 °C. (a) Ge_2Ph_4 growth/decay profiles recorded at 440 nm in the presence of 0-0.59 M THF; (b) $\Delta A_{440,0}/\Delta A_{440,Q}$ vs. [THF] from the data of (a).

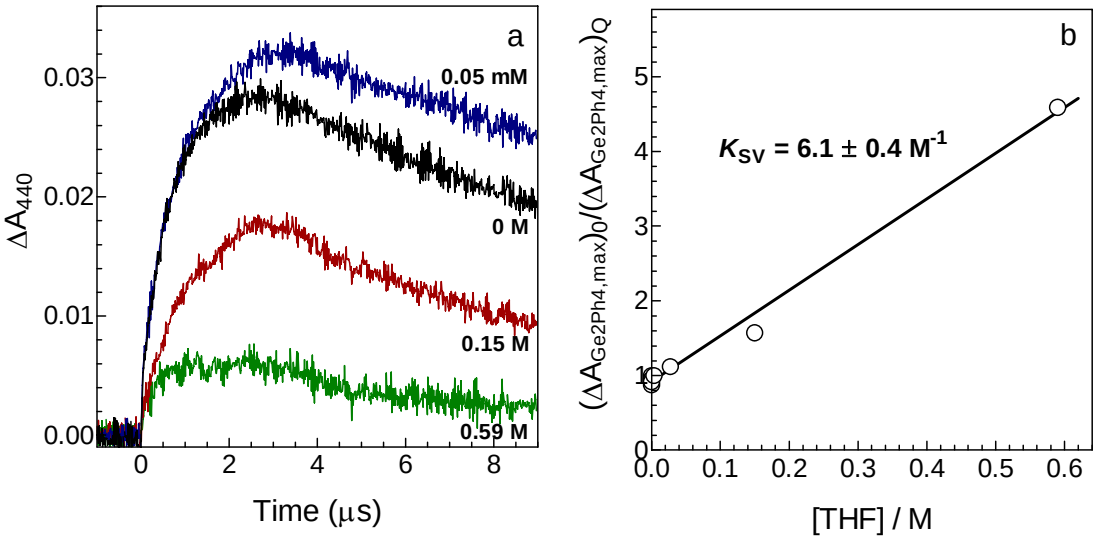

Figure S3. Additional kinetic data on the complexation of $GePh_2$ and MeOH in hexane at 25 ^{o}C. Plots of (a) the peak intensity ratios of the Ge_2Ph_4 signals $(\Delta A_{Ge2Ph4,max})_0/(\Delta A_{Ge2Ph4,max})_Q$ vs. [MeOH]; (b) the pseudo-first order rate constants for growth (k_{growth}) of the transient absorption at 350 nm due to the Ph_2Ge-MeOH complex (**2a**) vs [MeOH]. (c) the pseudo-first order rate constants for decay (k_{decay}) of Ge_2Ph_4 vs. [MeOH].

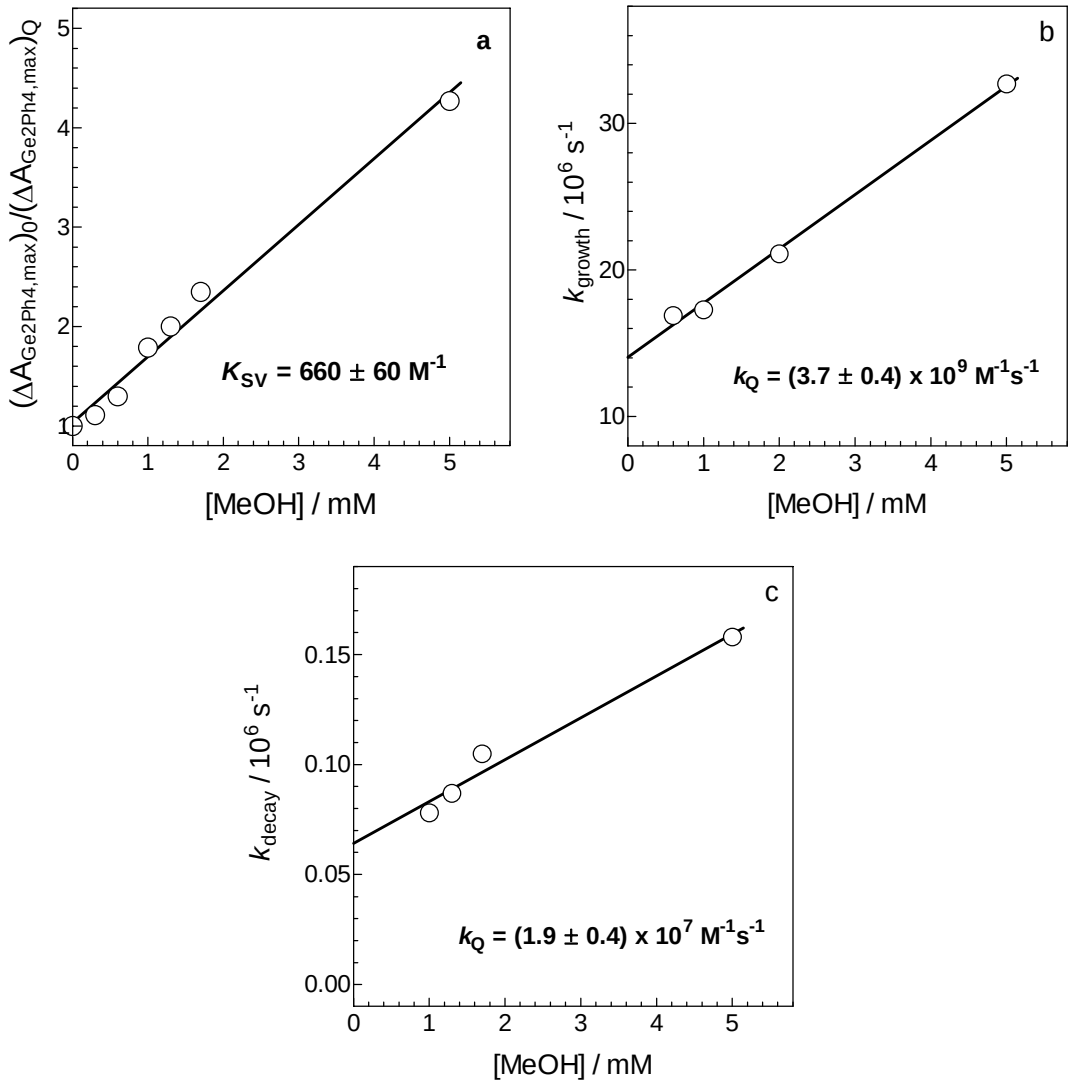

Figure S4. Kinetic data on the complexation of $GePh_2$ and t-BuOH in hexane at 25 ^oC. (a) corrected decay profiles for $GePh_2$ in the presence of t-BuOH; (b) growth/decay profiles for Ge_2Ph_4; (c) plots of k_{decay} (○) and $\Delta A_0/\Delta A_{res}$ (□) vs [t-BuOH] for $GePh_2$; (d) transient absorption spectra from **1a** in hexane containing 5 mM t-BuOH, recorded 0.24-0.26 μs (○) and 3.41-3.45 μs (□) after the laser pulse (the inset shows decay/growth profiles recorded at monitoring wavelengths of 340 and 440 nm); (e) plot of $(\Delta A_{Ge2Ph4,max})_0/(\Delta A_{Ge2Ph4,max})_Q$ vs [t-BuOH] for Ge_2Ph_4; (f) plot of k_{decay} vs [t-BuOH] for Ge_2Ph_4.

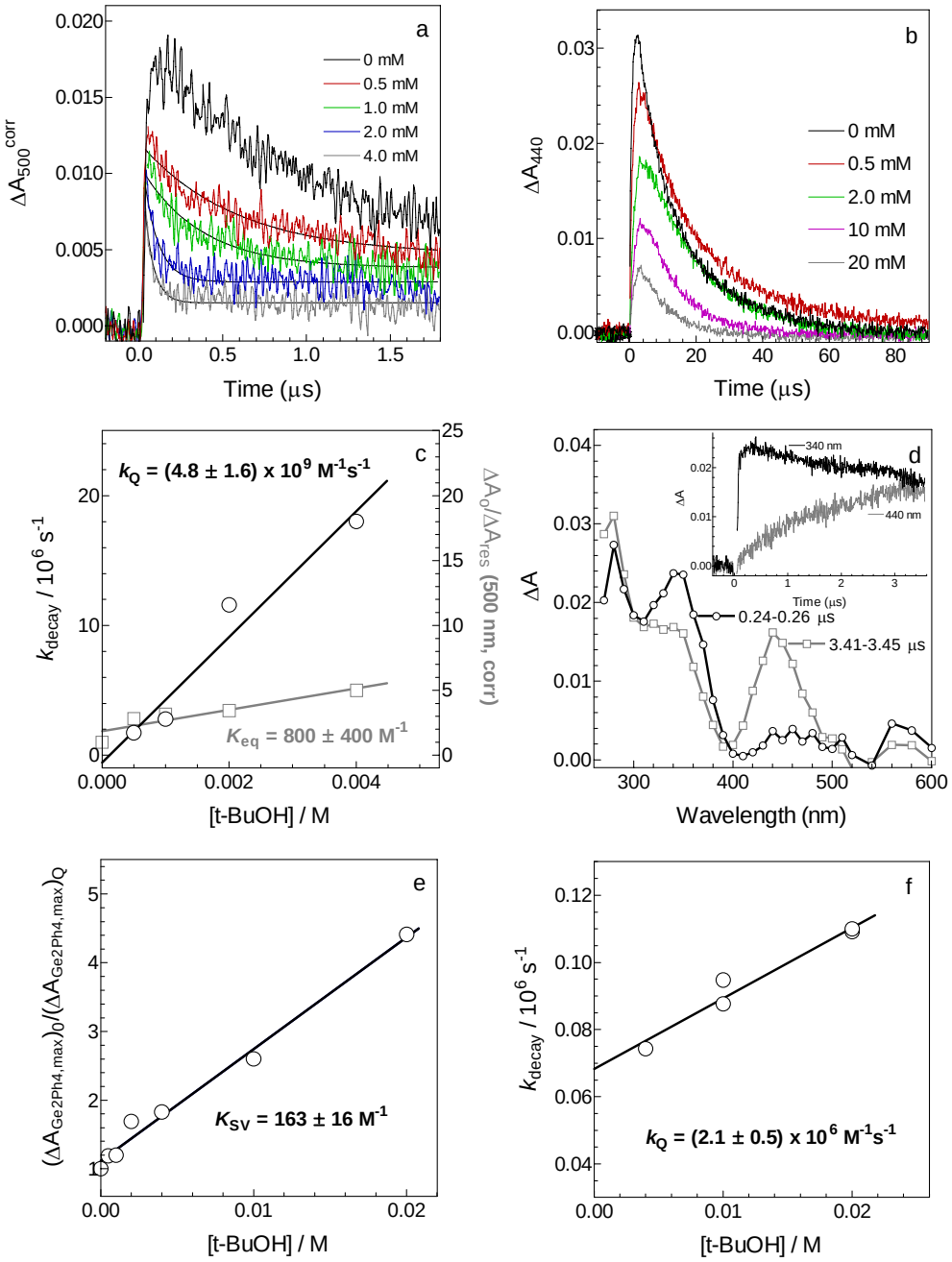

Figure S5. Transient decay and growth profiles for (a) $GeMes_2$ and (b) Ge_2Mes_4 in deoxygenated hexane containing THF. Transient absorption spectra of **1b** in hexane containing (c) 1 M and (d) 3.1 M THF, 0-0.32 μs (○) and 76-78 μs (□) after the laser pulse (the spectrum of $GeMes_2$ in hexane (·····), scaled to match the intensity of the 550 nm absorption bands in the THF spectra, is shown for comparison; the insets show decay/ growth profiles recorded at monitoring wavelengths of 280, 410, and 550 nm). (e) Plots of $(\Delta A_0)_0/(\Delta A_0)_Q$ vs. [THF] for $GeMes_2$ (○; 550 nm) and $(\Delta A_{Ge2Mes4,max})_0/(\Delta A_{Ge2Mes4,max})_Q$ vs. [THF] (□; 410 nm). (f) The spectrum of the Mes_2Ge-THF complex (**3c**), as the difference between the early spectrum of Fig S5d and that of free $GeMes_2$; the late spectrum of Fig S5d is included to show the relationship with the spectrum of Ge_2Mes_4.

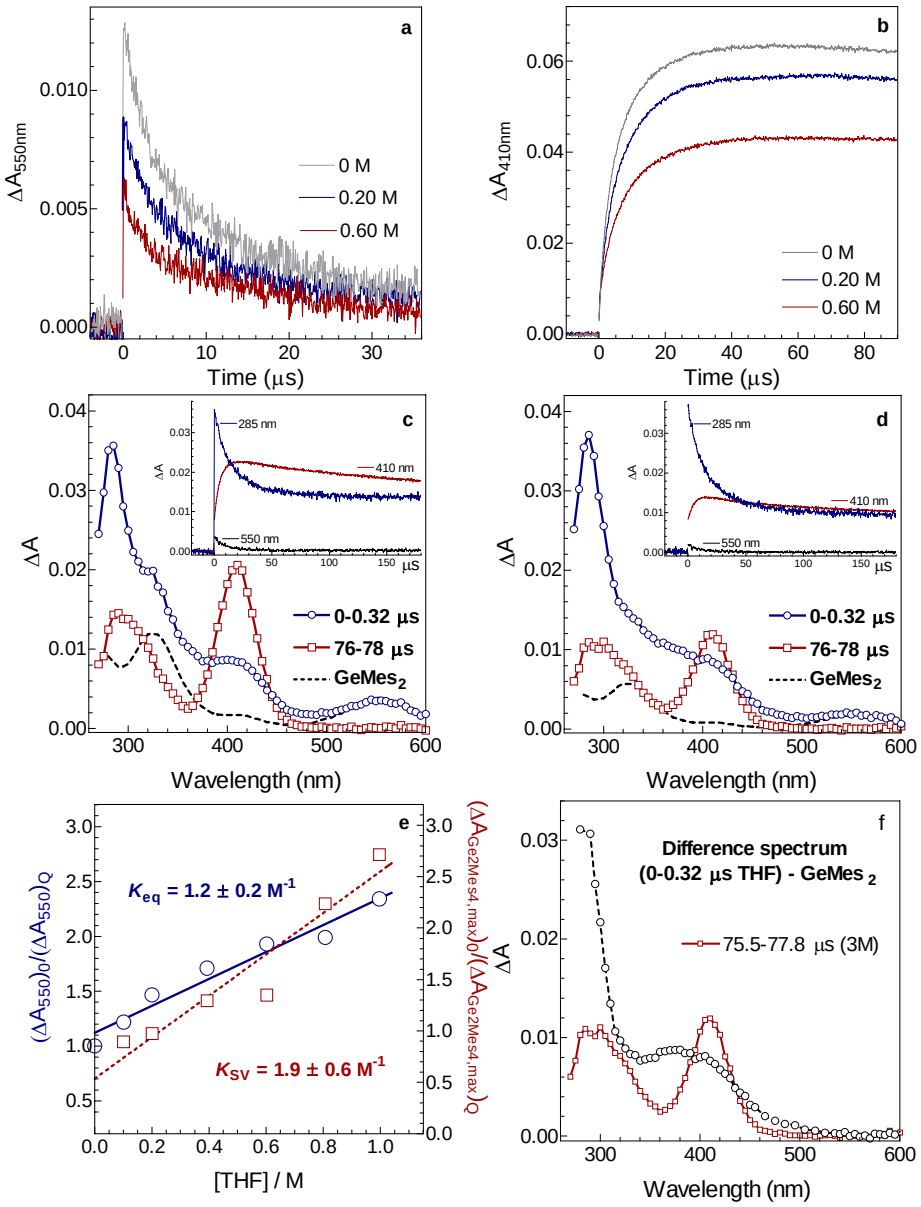

Figure S6. Additional data on the complexation of $GeMes_2$ and MeOH in hexane at 25 ^{o}C. (a) Transient absorption spectra recorded 0-0.64 μs (○) and 27.5-29.8 μs (□) after the laser pulse for a solution of **1c** in hexane containing 0.1 M MeOH; the inset shows growth/decay profiles recorded at 285 nm, 410 nm, and 550 nm; the dashed spectrum is that of $GeMes_2$ in hexane, scaled to match the intensity of the 550 nm absorption band in the early spectrum in the presence of MeOH (b) The spectrum of the Mes_2Ge-MeOH complex (**3a**; ○), extracted from the data of Fig S6a by subtracting the scaled spectrum of free $GeMes_2$ in hexane from the 0-0.64 μs spectrum in the presence of 0.1 M MeOH; the 27.5-29.8 μs spectrum of Fig S6a is included to show the relationship with the spectrum of Ge_2Mes_4. (c) Plot of $(\Delta A_0)_0/(\Delta A_0)_Q$ vs. [MeOH] for $GeMes_2$ and (d) $(\Delta A_{Ge2Mes4,max})_0/(\Delta A_{Ge2Mes4,max})_Q$ vs. [MeOH] for Ge_2Mes_4; the dotted lines are the fits of the data to a second order polynomial in [MeOH], the first order coefficients of which define the values of K_{eq} and K_{SV} that are reported.

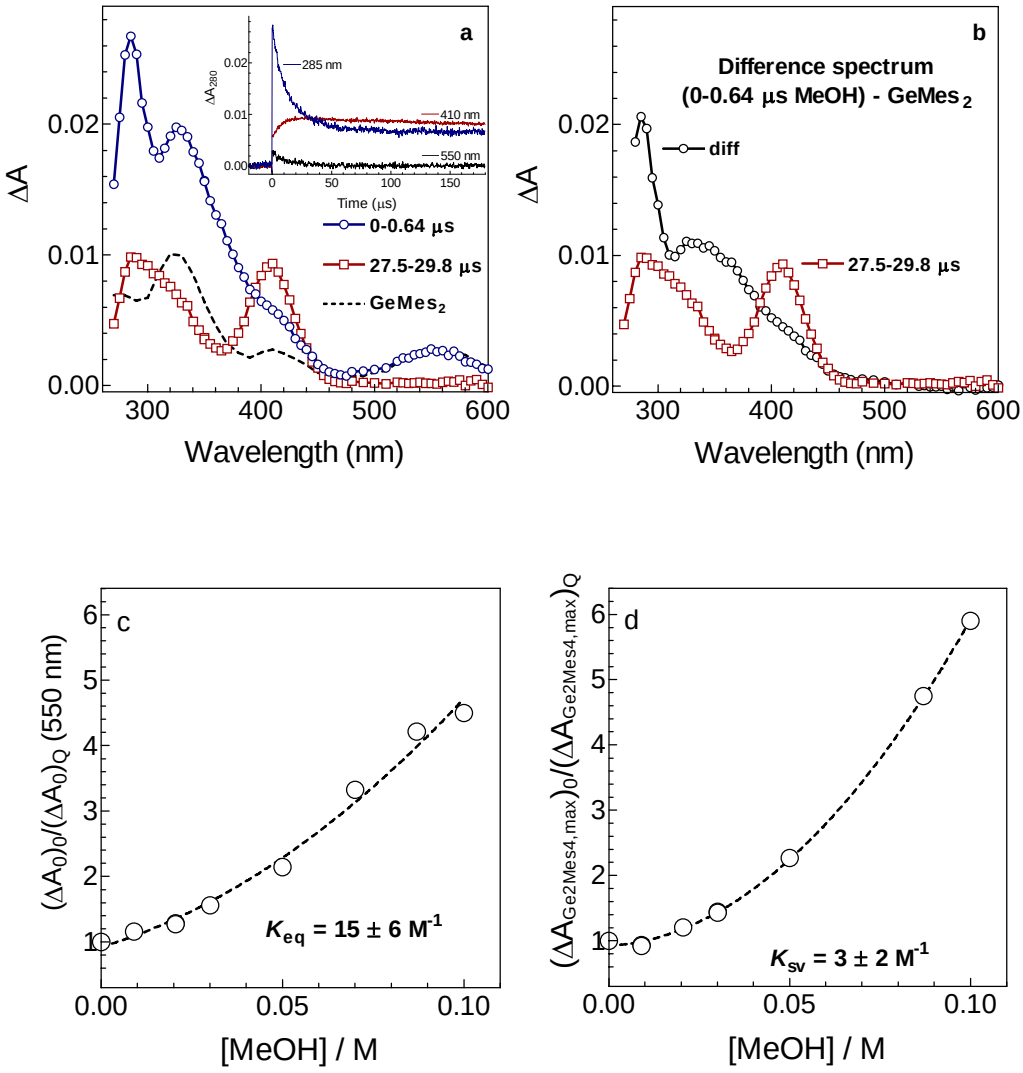

Figure S7. Additional data on the complexation of $GeMes_2$ and t-BuOH in hexane at 25 ^{o}C: (a) decay profiles for $GeMes_2$ in the presence of t-BuOH; (b) corresponding growth profiles for Ge_2Mes_4; (c) plots of $(\Delta A_0)_0/(\Delta A_0)_Q$ vs. [t-BuOH] for $GeMes_2$ (○; 550 nm) and $(\Delta A_{Ge2Mes4,max})_0/(\Delta A_{Ge2Mes4,max})_Q$ vs. [t-BuOH] for Ge_2Mes_4 (□; 410 nm).

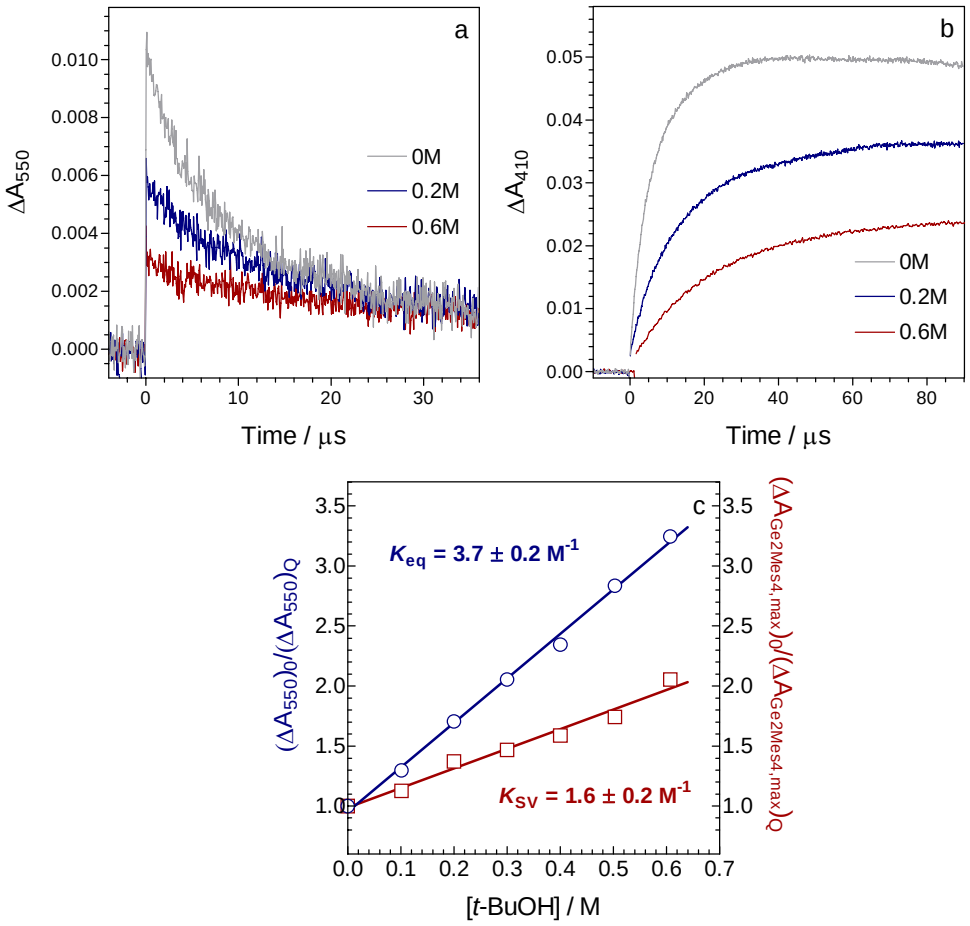

Figure S8. Transient decay and growth/decay profiles for (a) $GeMe_2$ and (b) Ge_2Me_4 in deoxygenated hexane containing THF, from laser flash photolysis of **1c**; (c) plots of k_{decay} (□) and $\Delta A_0/\Delta A_{res}$ (○) vs [THF]. The solid lines in (a) are the fits of the data to 2nd order (0 mM) or 1st-order kinetics (0.198 – 1.1 mM; eqn 6), while those in (c) are the linear least squares fits of the data to equations 7 and 8, respectively.

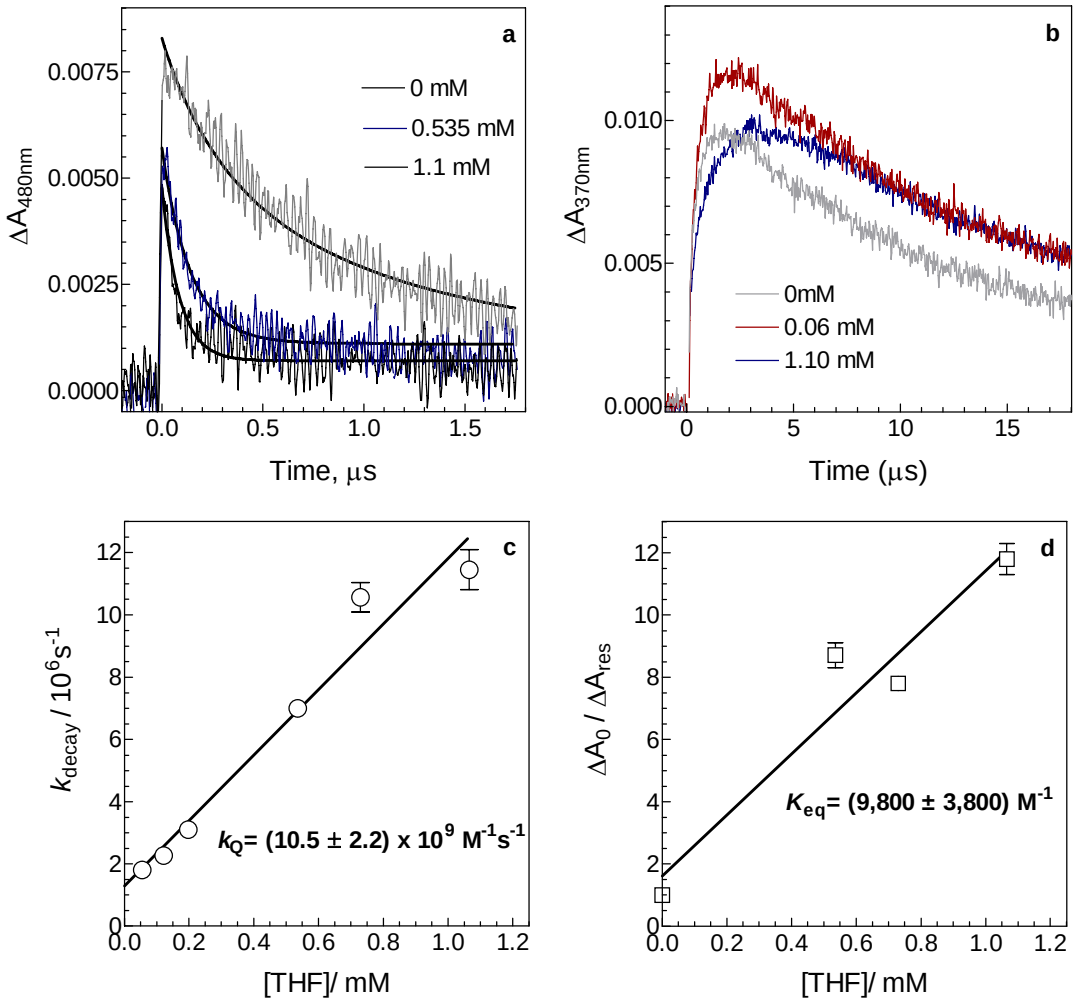

Figure S9. (a) Decay profiles for $GeMe_2$ in hexane containing 0, 1.9 and 4.3 mM MeOH; (b) growth/decay profiles for Ge_2Me_4 in hexane containing 0 - 4.30 mM MeOH; (c) plots of $(\Delta A_0)_0/(\Delta A_0)_Q$ for the germylene (○) and digermene (□) signals vs [MeOH]. (d) plot of k_{decay} vs. [MeOH] for Ge_2Me_4, from an experiment carried out at higher laser intensity. (e) transient absorption spectra of **1c** in hexane containing 54 mM MeOH, recorded 0.13-0.16 μs and 8.58-8.69 μs after the laser pulse, with the spectrum of $GeMe_2$ in hexane (⋯) included for comparison; the inset shows the decay trace at 295 nm from the data set used to construct the spectra.

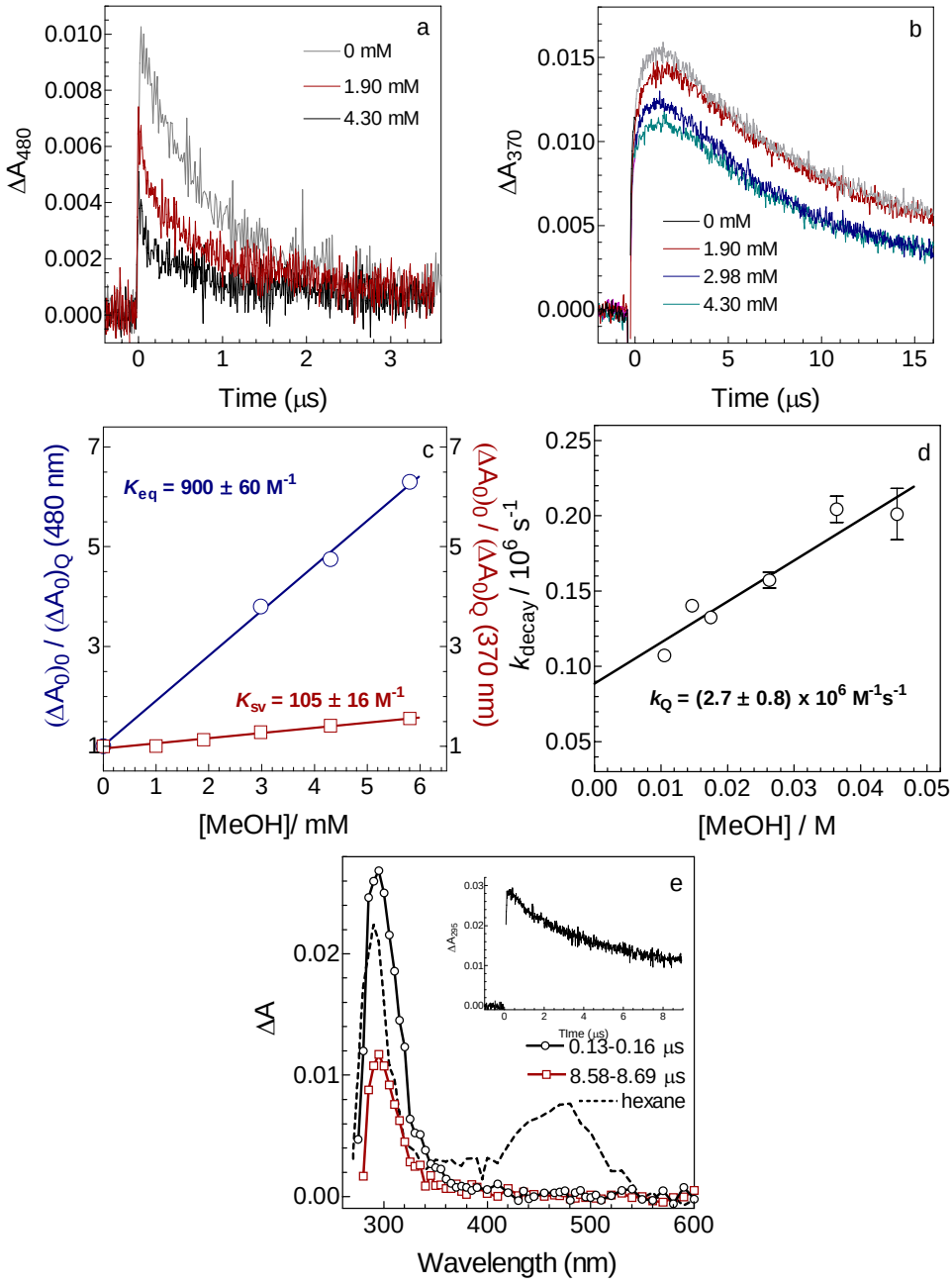

Figure S10. (a) Decay profiles for $GeMe_2$ in hexane containing 0, 2.0 and 5.1 mM t-BuOH. (b) Corresponding growth/decay profiles for Ge_2Me_4. (c) Transient absorption spectra recorded in hexane containing 8 mM t-BuOH, 128-192 ns and 8.86-8.98 μs after the laser pulse; the inset shows decay/growth profiles recorded at monitoring wavelengths of 320, 370, and 480 nm. (d) Plots of $(\Delta A_0)_0/(\Delta A_0)_Q$ vs [t-BuOH] for $GeMe_2$ (□) and $(\Delta A_{max})_0/(\Delta A_{max})_Q$ vs [t-BuOH] for Ge_2Me_4 (○). (e) Plot of k_{decay} vs. [t-BuOH] for Ge_2Me_4 over the 0-0.1 M range in alcohol concentration.