Supporting Information for

Electronic and Steric Effects on the Lewis Acidities of Transient Silylenes and Germylenes – Equilibrium Constants for Complexation with Chalcogen and Pnictogen Donors.

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Table S1. Experimental Gibbs Free Energies for Lewis Acid-Base Complexation of Silylenes and Germylenes with Methanol (MeOH, Diethyl ether (Et_2O), and Tetrahydrofuran (THF) in Hexanes at 25 °C (in kcal mol^{-1}; reference state, 1 M Hexanes, 25 °C).

	Δ*G* (kcal mol^{-1})					
	$SiMe_2$	$SiPh_2$	$SiMes_2$	$GeMe_2$	$GePh_2$	$GeMes_2$
MeOH	*a*	*a*	*a*	-4.0 ± 0.1	-4.8 ± 0.2	-1.6 ± 0.3
Et_2O	-4.2 ± 0.1	-5.2 ± 0.1	+0.1 ± 0.1	-2.8 ± 0.1	-3.0 ± 0.1	+1.7 ± 0.4
THF	*a,b*	*a,b*	-0.5 ± 0.1	-5.4 ± 0.3	-5.9 ± 0.1	-0.1 ± 0.1
THT	*a,b*	*a,b*	-4.3 ± 0.1	*a,b*	*a,b*	-4.1 ± 0.1
Et_2NH	*a,b*	*a,b*	-5.2 ± 0.1	*a,b*	*a,b*	-3.7 ± 0.1
Et_3N	*a,b*	*a,b*	-2.9 ± 0.4	*a,b*	*a,b*	≥ -2.7 [a,c]
Et_3P	*a,b*	*a,b*	*a,b*	*a,b*	*a,b*	*a,b*
Cy_3P [i]	*a,b*	*a,b*	-6.0 ± 0.1	*a,b*	*a,b*	-4.7 ± 0.2

[a] K_C indeterminable. [b] Upper limit is -6.0 kcal mol^{-1}. [c] Lower limit.

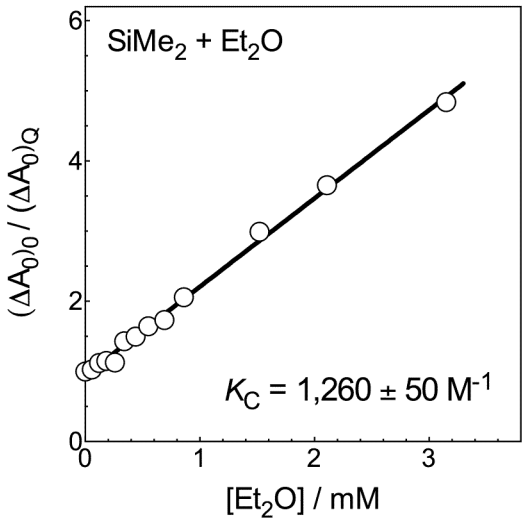

Figure S1. Plot of $(\Delta A_0)_0 / (\Delta A_0)_Q$ for complexation of $SiMe_2$ with Et_2O (Hexanes, 25 °C).

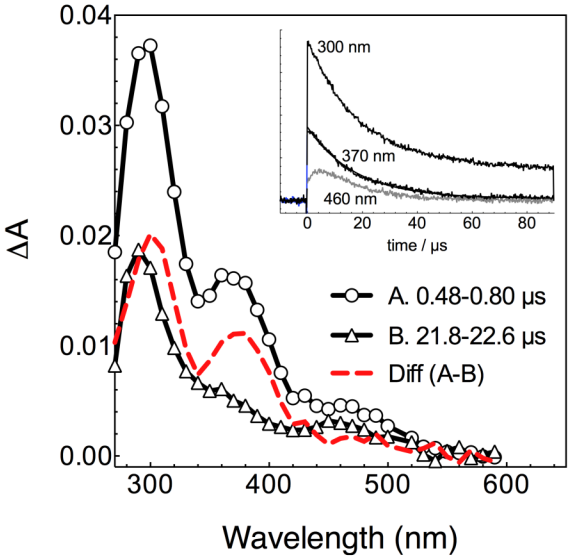

Figure S2. Time-resolved UV-vis spectra recorded by laser photolysis of $SiPh_2$ precursor **2** in hexanes containing 0.1 M Et_2O. The corresponding plots of k_{decay} and $(\Delta A_0)_0 / (\Delta A_{res})_Q$ vs. [Q] are shown in Figure 1b of the paper.

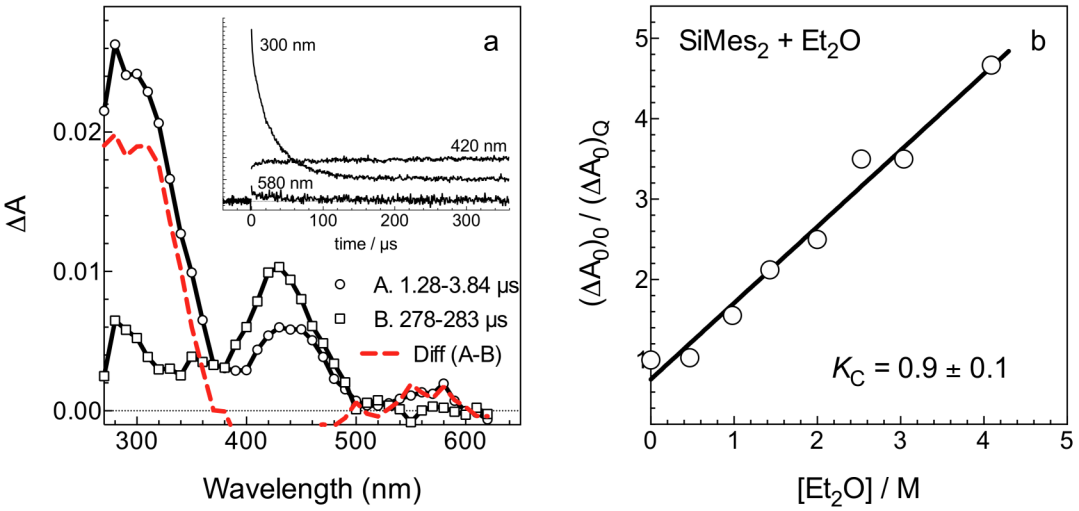

Figure S3. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $SiMes_2$ precursor **3** in Et_2O, and (b) plot of $(\Delta A_0)_0 / (\Delta A_0)_Q$ vs. $[Et_2O]$.

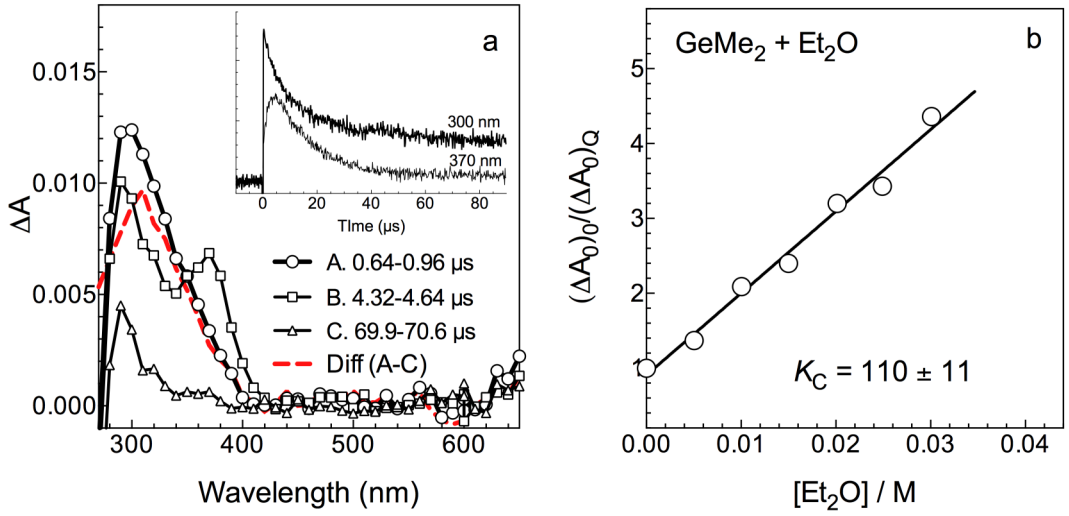

Figure S4. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $GeMe_2$ precursor **4** in hexanes containing 0.1 M Et_2O, and (b) plot of $(\Delta A_0)_0 / (\Delta A_0)_Q$ vs. $[Et_2O]$.

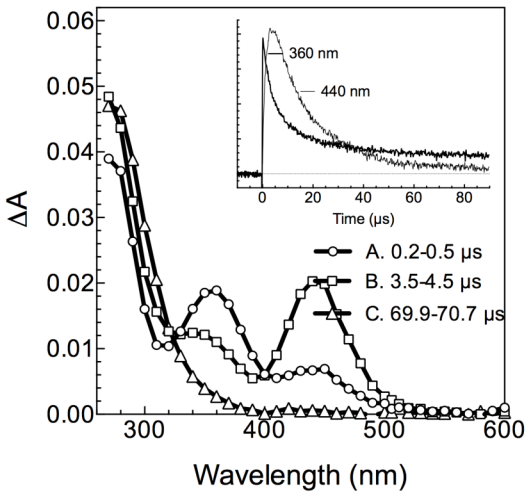

Figure S5. Time-resolved UV-vis spectra recorded by laser photolysis of $GePh_2$ precursor **5** in hexanes containing 0.1 M Et_2O. The corresponding plot of $(\Delta A_0)_0 / (\Delta A_{res})_Q$ vs. [Q] is shown in Figure 1c of the paper.

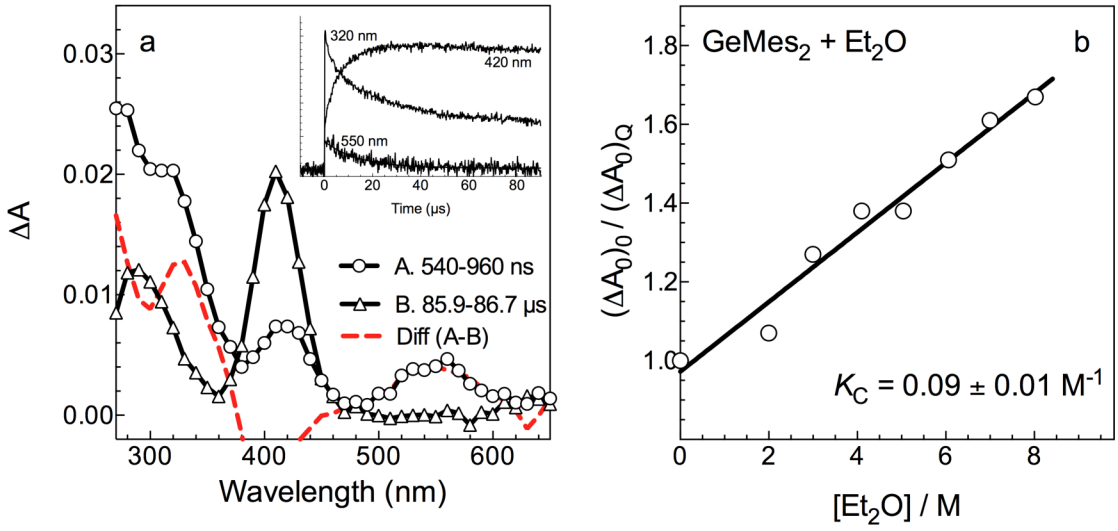

Figure S6. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $GeMes_2$ precursor **6** in Et_2O, and (b) plot of $(\Delta A_0)_0 / (\Delta A_0)_Q$ vs. $[Et_2O]$ in Et_2O-hexanes mixtures.

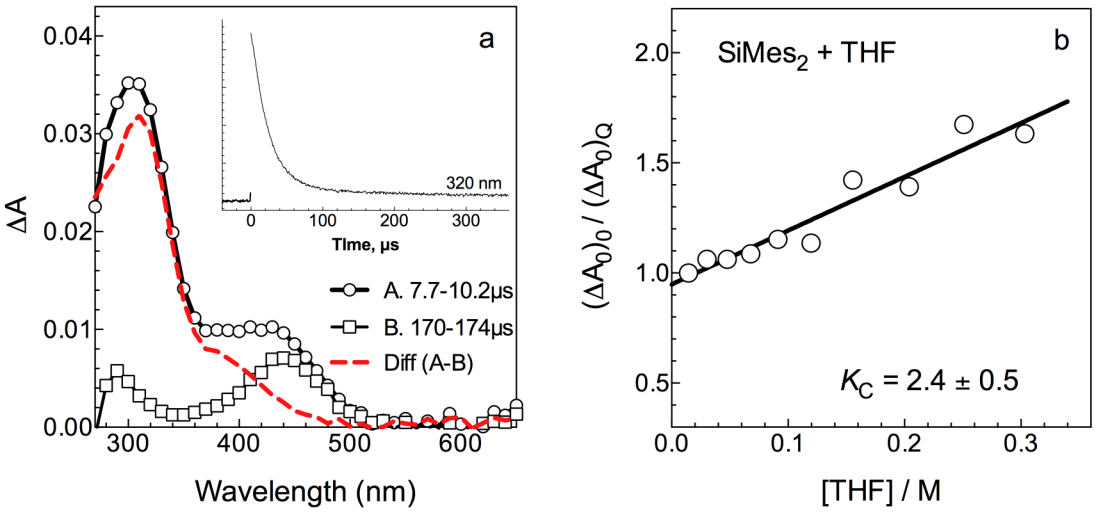

Figure S7. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $SiMes_2$ precursor **6** in THF, and (b) plot of $(\Delta A_0)_0 / (\Delta A_0)_Q$ vs. [THF] for quenching of $SiMes_2$ by THF in hexanes at 25 °C.

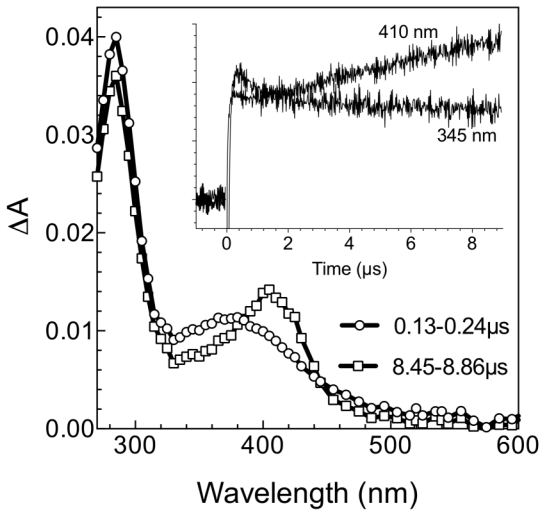

Figure S8. Time-resolved UV-vis spectra recorded by laser photolysis of $GeMes_2$ precursor **6** in THF.

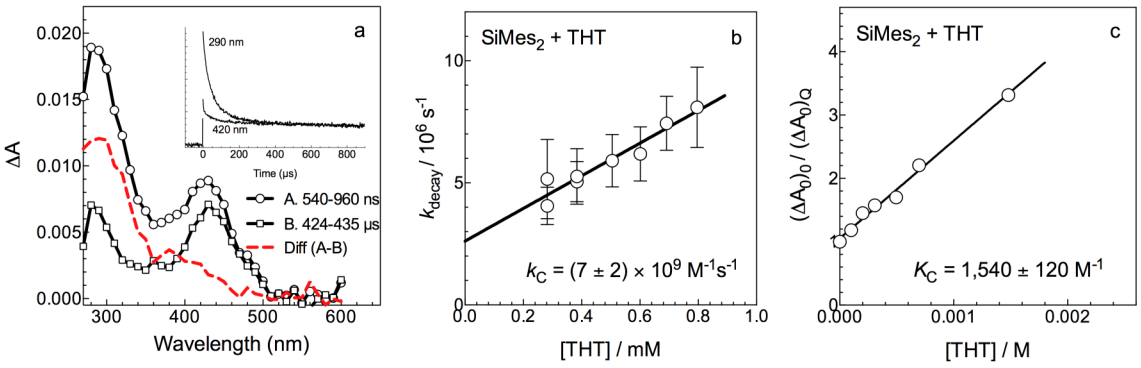

Figure S9. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $SiMes_2$ precursor **3** in hexanes containing 0.01 M THT, and plots of (b) k_{decay} and (c) $(\Delta A_0)_0 / (\Delta A_0)_Q$ vs. [THT].

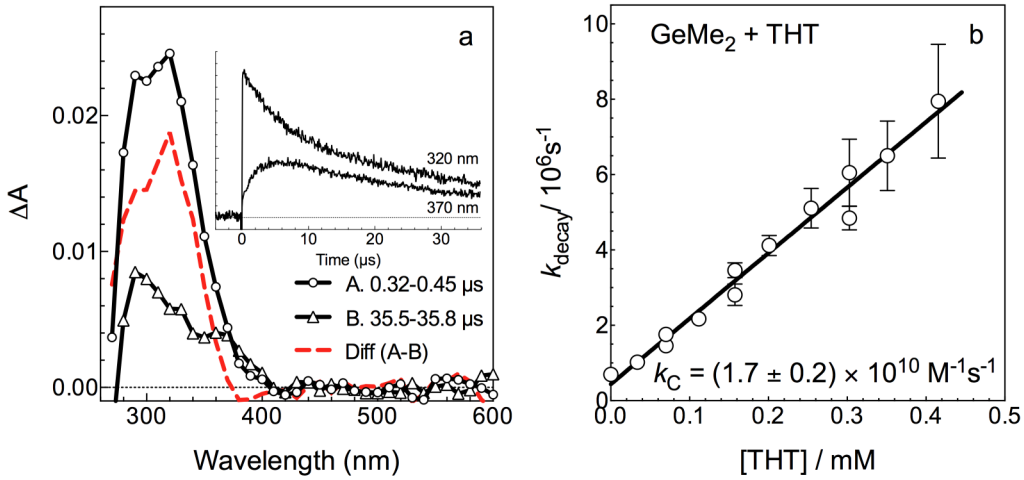

Figure S10. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $GeMe_2$ precursor **4** in hexanes containing 0.01 M THT, and (b) plot of k_{decay} vs. [THT].

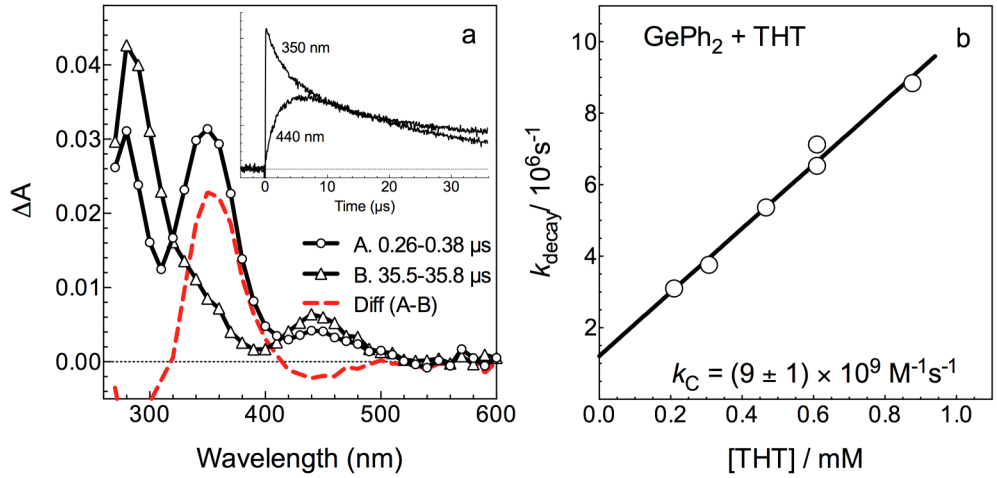

Figure S11. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $GePh_2$ precursor **5** in hexanes containing 0.01 M THT, and (b) plot of k_{decay} vs. [THT].

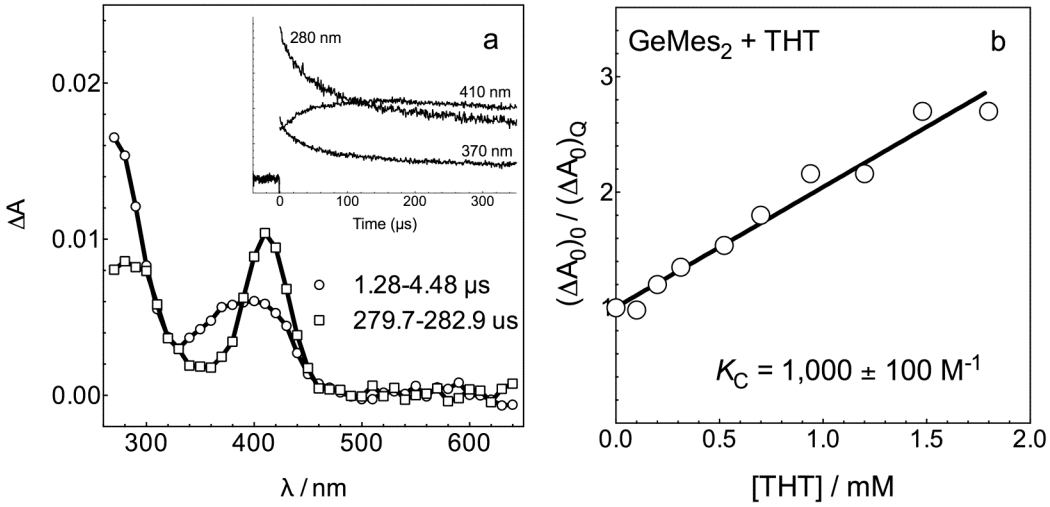

Figure S12. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $GeMes_2$ precursor **6** in hexanes containing 0.0054 M THT, and (b) plot of $(\Delta A_0)_0 / (\Delta A_0)_Q$ vs. [THT].

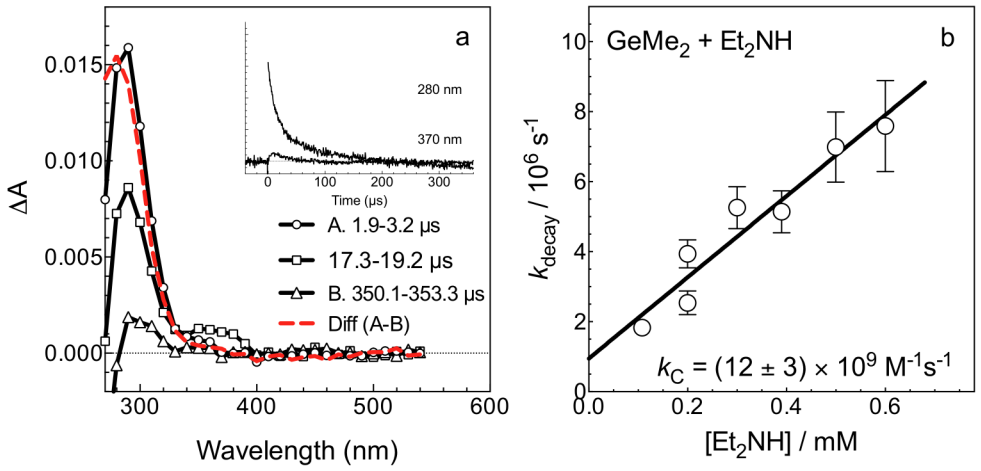

Figure S13. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $GeMe_2$ precursor **4** in hexanes containing 0.0053 M Et_2NH, and (b) plot of k_{decay} vs. [Et_2NH].

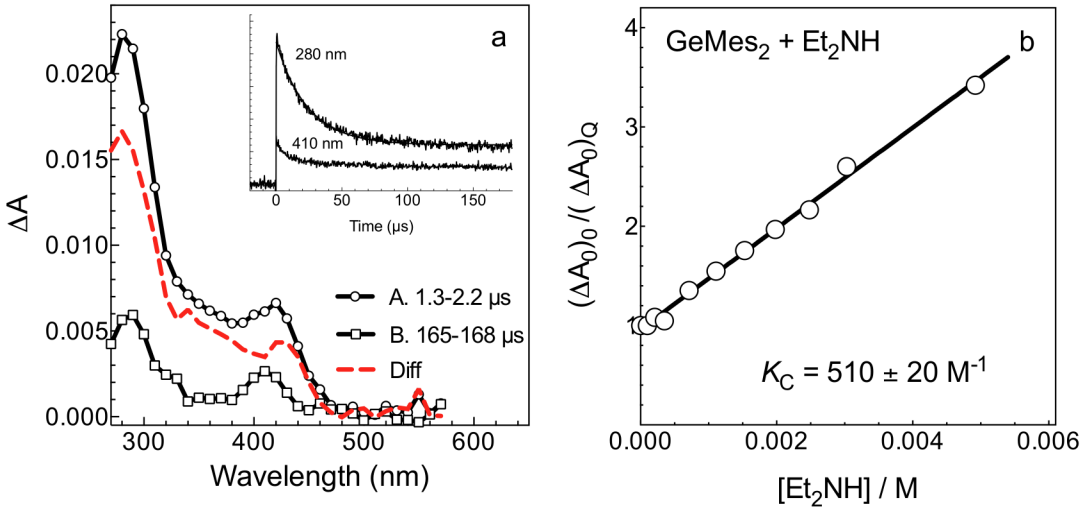

Figure S14. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $GeMes_2$ precursor **6** in hexanes containing 0.02 M Et_2NH, and (b) plot of $(\Delta A_0)_0 / (\Delta A_0)_Q$ vs. [Et_2NH].

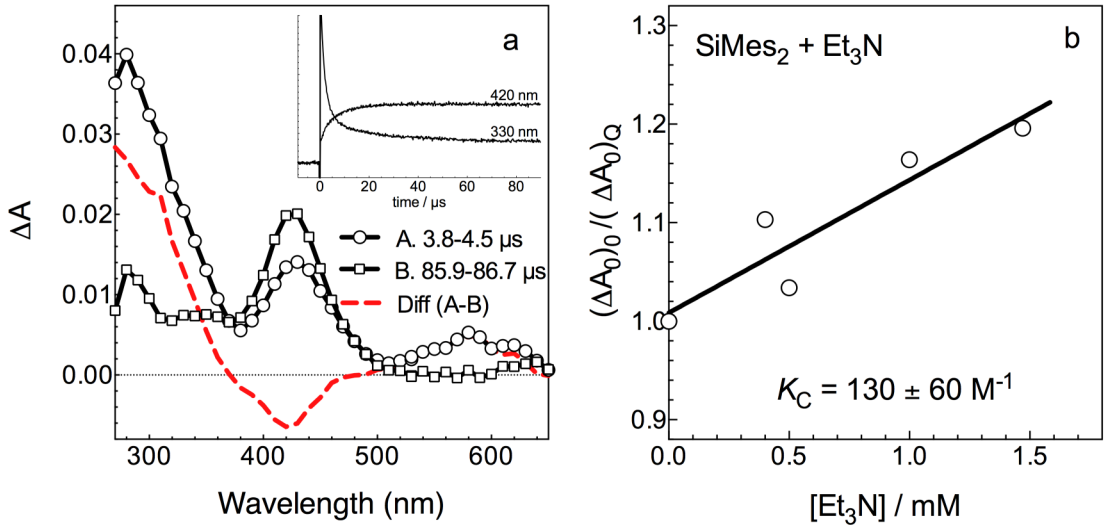

Figure S15. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $SiMes_2$ precursor **3** in hexanes containing 1.5 mM Et_3N, and (b) plot of $(\Delta A_0)_0$ / $(\Delta A_0)_Q$ vs. $[Et_3N]$.

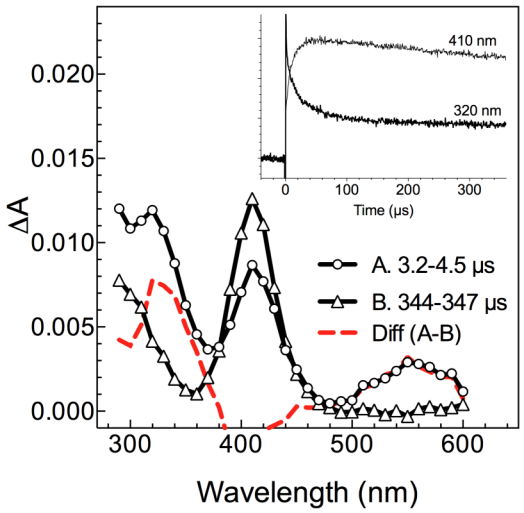

Figure S16. Time-resolved UV-vis spectra recorded by laser photolysis of $GeMes_2$ precursor **6** in hexanes containing 1.3 mM Et_3N (complex undetectable).

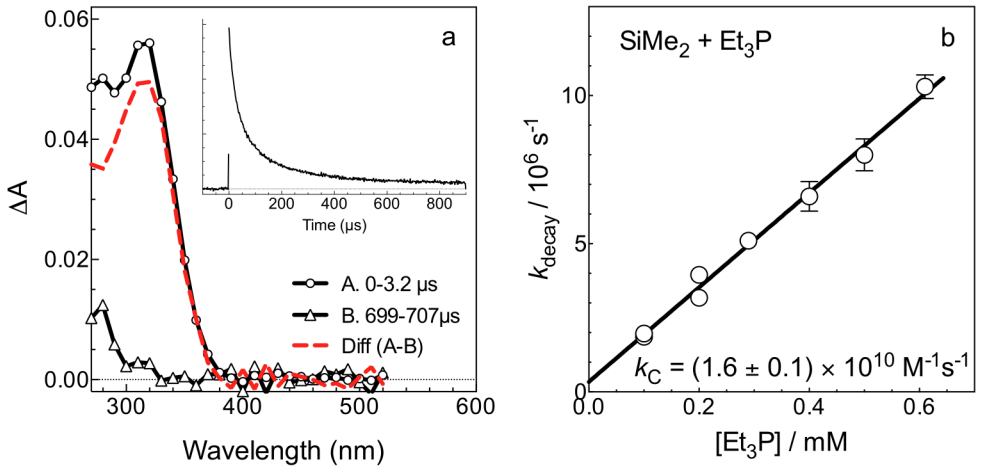

Figure S17. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $SiMe_2$ precursor **1** in hexanes containing 5.6 mM Et_3P, and (b) plot of k_{decay} vs. [Et_3P].

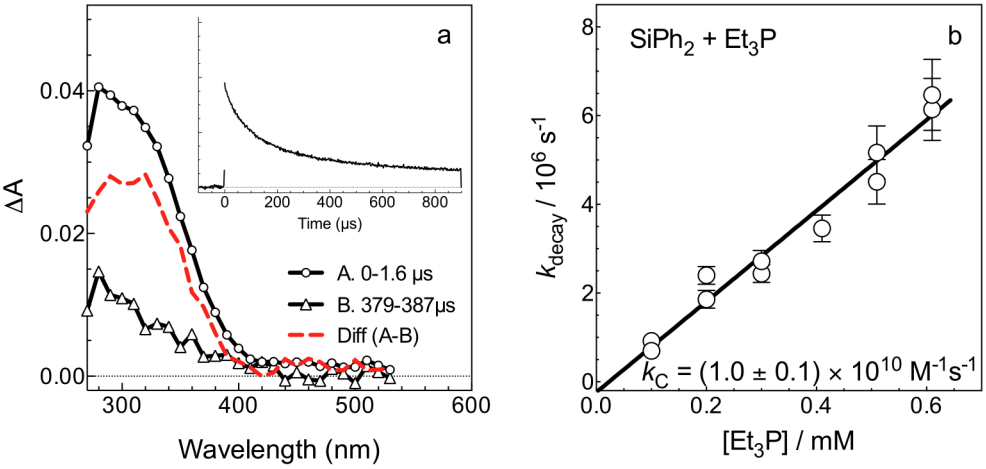

Figure S18. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $SiPh_2$ precursor **2** in hexanes containing 5.6 mM Et_3P, and (b) plot of k_{decay} vs. [Et_3P].

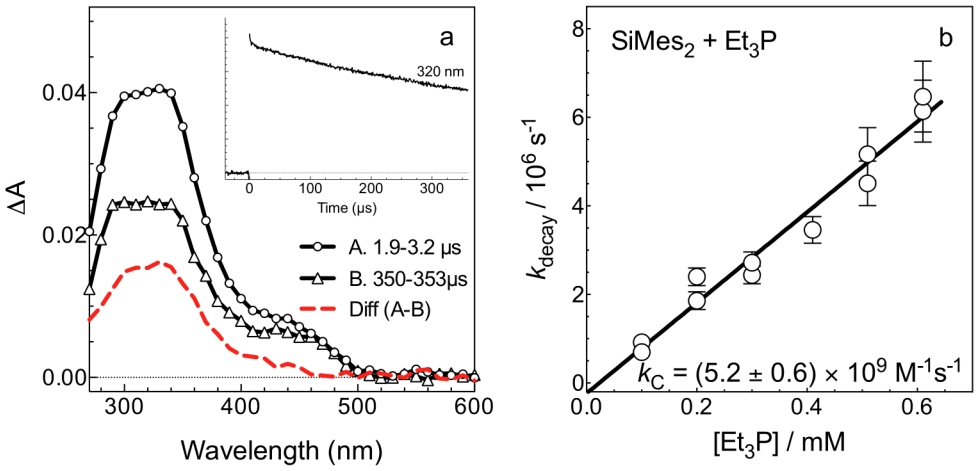

Figure S19. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $SiMes_2$ precursor **3** in hexanes containing 3.5 mM Et_3P, and (b) plot of k_{decay} vs. [Et_3P].

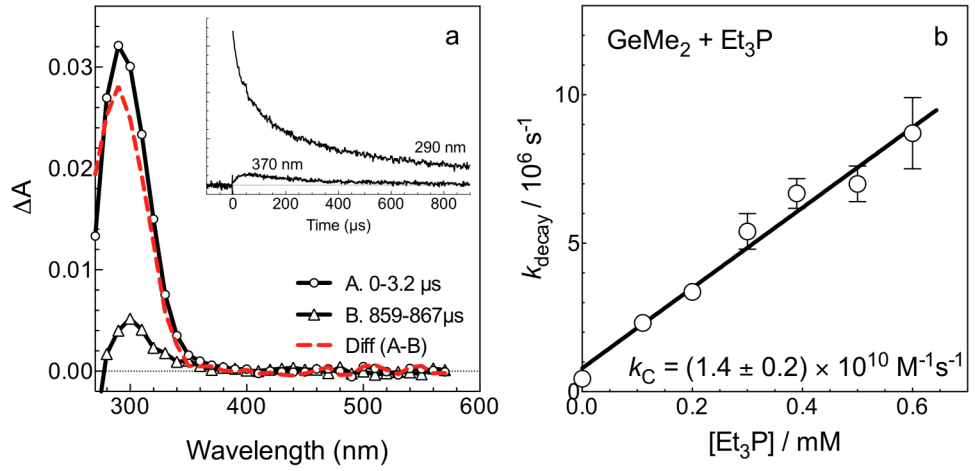

Figure S20. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $GeMe_2$ precursor **4** in hexanes containing 4.7 mM Et_3P, and (b) plot of k_{decay} vs. [Et_3P].

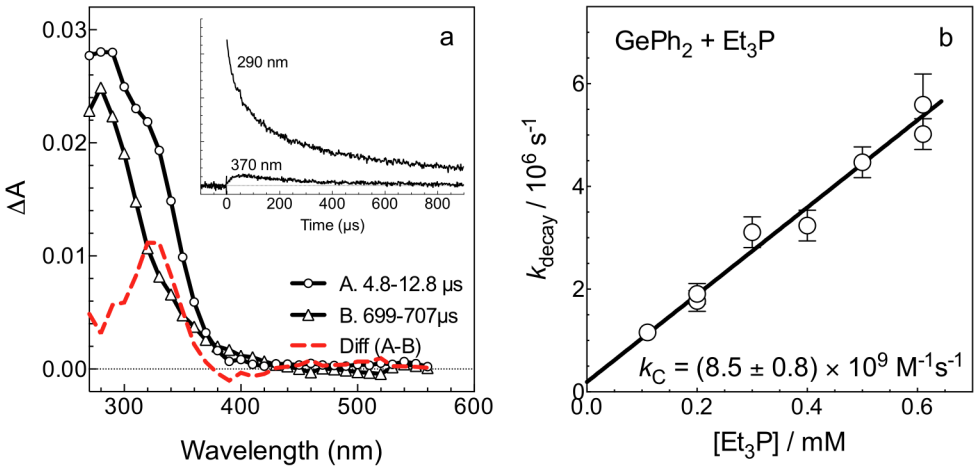

Figure S21. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $GePh_2$ precursor **5** in hexanes containing 4.8 mM Et_3P, and (b) plot of k_{decay} vs. [Et_3P].

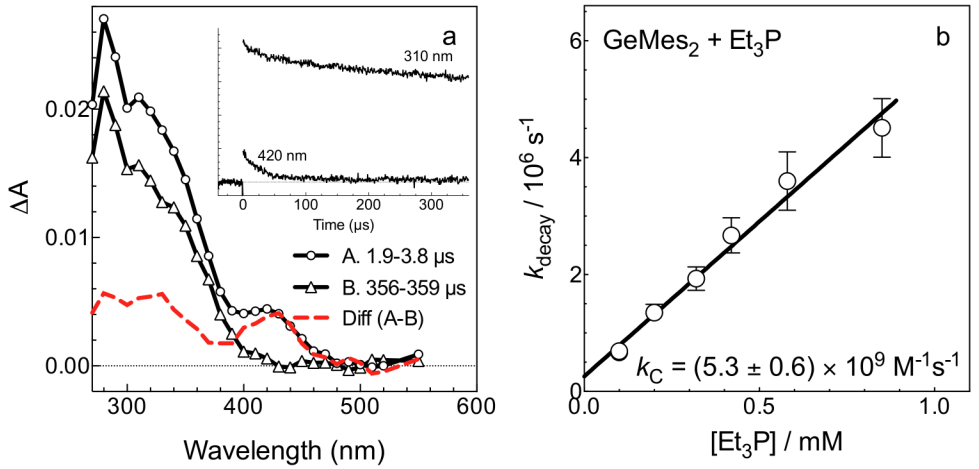

Figure S22. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $GeMes_2$ precursor **6** in hexanes containing 4.8 mM Et_3P, and (b) plot of k_{decay} vs. [Et_3P].

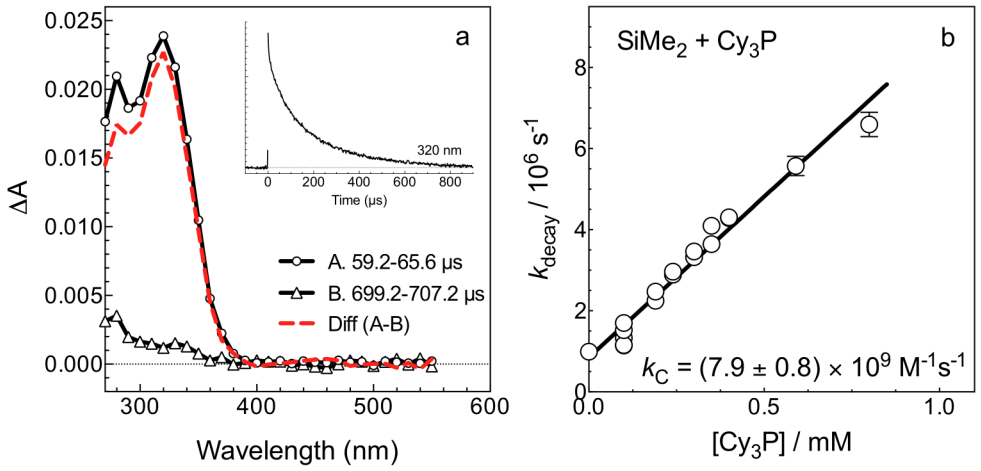

Figure S23. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $SiMe_2$ precursor **1** in hexanes containing 3.8 mM Cy_3P, and (b) plot of k_{decay} vs. [Cy_3P].

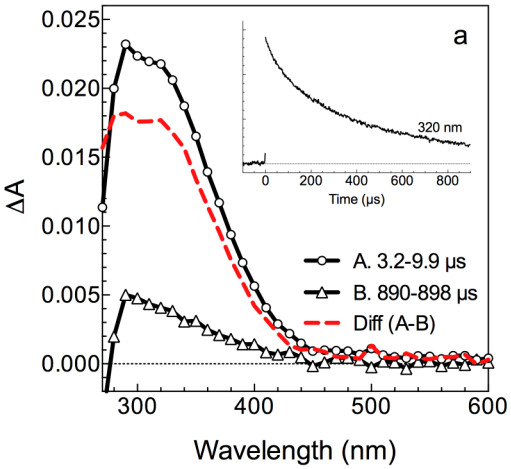

Figure S24. Time-resolved UV-vis spectra recorded by laser photolysis of $SiPh_2$ precursor **2** in hexanes containing 2.0 mM Cy_3P. The corresponding plot of k_{decay} vs. [Cy_3P] is shown in Figure 1a of the paper.

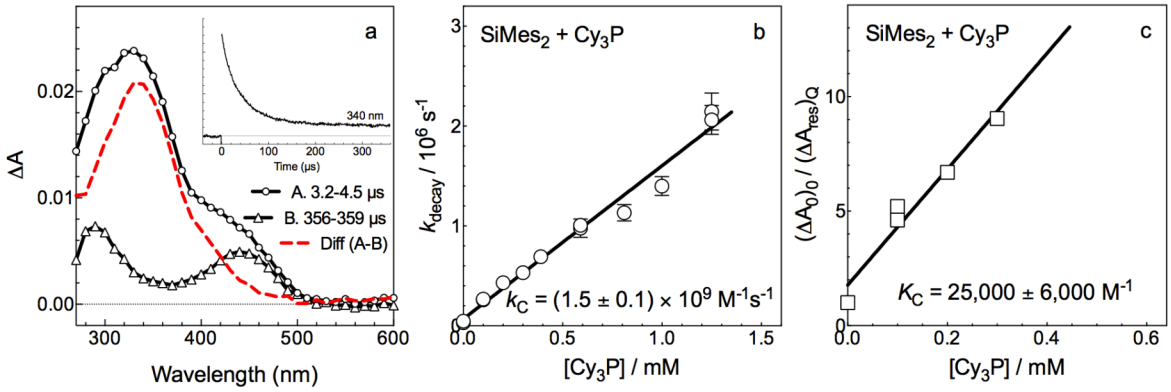

Figure S25. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $SiMes_2$ precursor **3** in hexanes containing 2.8 mM Cy_3P and plots of (b) k_{decay} and (c) $(\Delta A_0)_0$ / $(\Delta A_{res})_Q$ vs. $[Cy_3P]$.

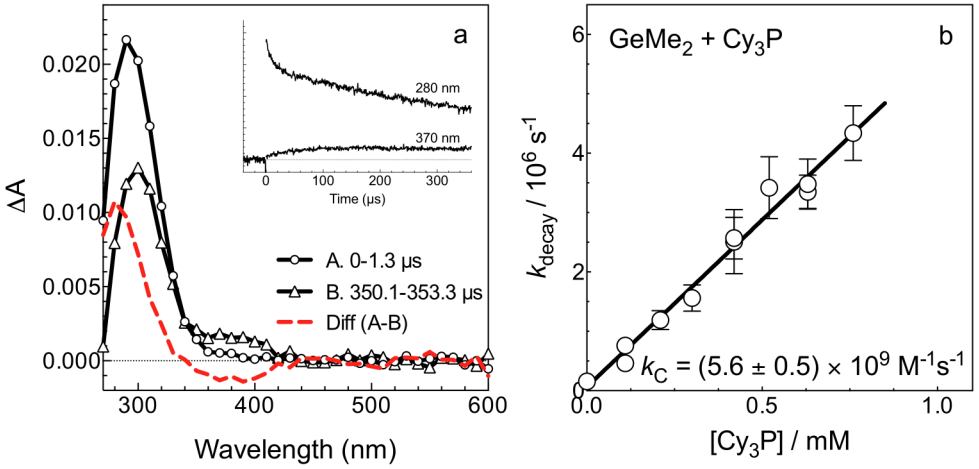

Figure S26. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $GeMe_2$ precursor **4** in hexanes containing 1.4 mM Cy_3P, and (b) plot of k_{decay} vs. $[Cy_3P]$.

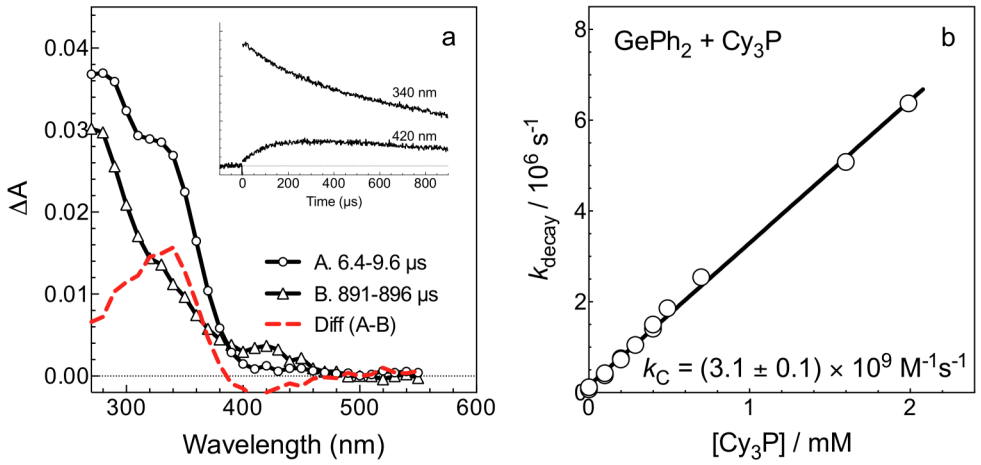

Figure S27. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $GePh_2$ precursor **5** in hexanes containing 3.6 mM Cy_3P, and (b) plot of k_{decay} vs. [Cy_3P].

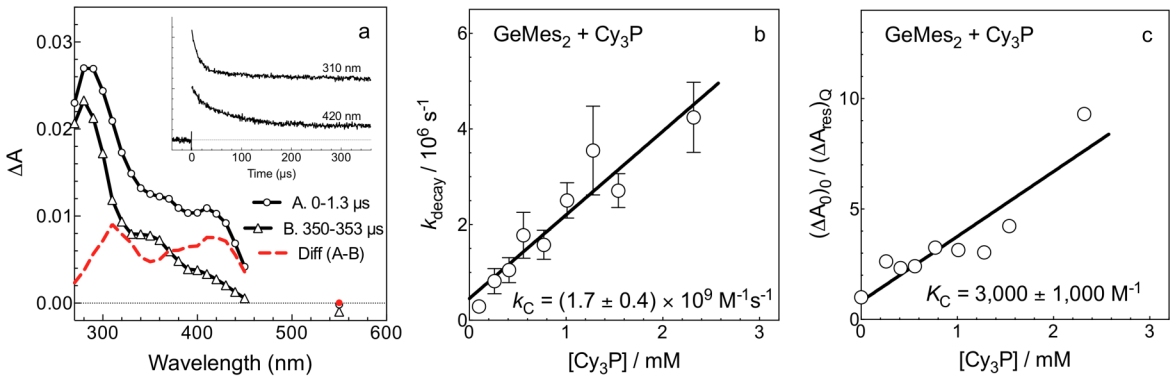

Figure S28. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $GeMes_2$ precursor **6** in hexanes containing 2.8 mM Cy_3P and plots of (b) k_{decay} and (c) $(\Delta A_0)_0$ / $(\Delta A_{res})_Q$ vs. [Cy_3P].

Calculated (G4) Thermochemical Data and Geometries

Theoretical calculations were carried out at the Gaussian-4 level of theory using the Gaussian09 suite of programs.[1] Calculated thermochemical data and optimized geometries of $SiMe_2$ and its complex with MeOH were taken from ref. 2. Those for $GeMe_2$ and the other complexes listed in Table 4 of the paper are summarized below. All calculations refer to a temperature of 298.15 K and 1.0 atm pressure.

$SiMe_2$+Me_2O complex (gauche)

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.151473	E(Thermal)=	0.162338
E(CCSD(T))=	-523.057681	E(Empiric)=	-0.131993
DE(Plus)=	-0.019265	DE(2DF)=	-0.273006
E(Delta-G3XP)=	-0.635776	DE(HF)=	-0.031742
G4(0 K)=	-523.997991	G4 Energy=	-523.987125
G4 Enthalpy=	-523.986181	G4 Free Energy=	-524.034012

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.380017	0.617439	1.224924
2	6	0	-2.123792	-0.389538	-0.806774
3	1	0	-0.500590	1.090166	1.658617
4	1	0	-2.203016	1.339489	1.178141
5	1	0	-1.679188	-0.244590	1.832029
6	1	0	-1.736295	-0.680616	-1.782790
7	1	0	-2.930995	0.343742	-0.914506
8	1	0	-2.495645	-1.271473	-0.271594
9	14	0	0.924700	-0.299742	-0.744975
10	6	0	1.327324	-1.352514	0.821881
11	1	0	2.395541	-1.607338	0.759574
12	1	0	1.180911	-0.854425	1.788764
13	1	0	0.788644	-2.306694	0.837020
14	6	0	1.661287	1.387142	-0.175709
15	1	0	2.741653	1.332167	-0.375712
16	1	0	1.283584	2.225110	-0.771449
17	1	0	1.556515	1.638883	0.887753
18	8	0	-1.031966	0.202099	-0.097764

$SiMe_2$+Me_2O complex (anti)

E(ZPE)=	0.151938	E(Thermal)=	0.162573
E(CCSD(T))=	-523.058312	E(Empiric)=	-0.131993
DE(Plus)=	-0.019858	DE(2DF)=	-0.273036
E(Delta-G3XP)=	-0.635347	DE(HF)=	-0.031578
G4(0 K)=	-523.998185	G4 Energy=	-523.987550
G4 Enthalpy=	-523.986606	G4 Free Energy=	-524.033515

Number	Atomic #	Type	X	Y	Z
1	6	0	1.785538	-1.187378	-0.031267
2	6	0	1.785526	1.187394	-0.031284
3	1	0	2.078405	-1.257235	1.022743
4	1	0	1.152960	-2.033103	-0.295967
5	1	0	2.676070	-1.174016	-0.668653
6	1	0	1.152981	2.033110	-0.296096
7	1	0	2.676111	1.173984	-0.668595
8	1	0	2.078305	1.257319	1.022745
9	14	0	-0.901725	-0.000005	0.734645
10	6	0	-1.539205	-1.449653	-0.368977
11	1	0	-1.216305	-2.438603	-0.025808
12	1	0	-2.635595	-1.442510	-0.281703
13	1	0	-1.304911	-1.350996	-1.435868
14	6	0	-1.539233	1.449645	-0.368958
15	1	0	-2.635633	1.442377	-0.281814
16	1	0	-1.216470	2.438609	-0.025703
17	1	0	-1.304810	1.351062	-1.435828
18	8	0	1.020909	0.000003	-0.263946

$SiMe_2$+Me_2S complex (gauche)

E(ZPE)=	0.147410	E(Thermal)=	0.158764
E(CCSD(T))=	-845.682947	E(Empiric)=	-0.131993
DE(Plus)=	-0.014529	DE(2DF)=	-0.279208
E(Delta-G3XP)=	-0.899744	DE(HF)=	-0.032875
G4(0 K)=	-846.893886	G4 Energy=	-846.882532
G4 Enthalpy=	-846.881588	G4 Free Energy=	-846.930386

Number	Atomic #	Type	X	Y	Z
1	6	0	2.064867	-1.020868	-0.554862
2	6	0	1.447688	1.061326	1.195272
3	1	0	1.846479	-1.503503	-1.507577
4	1	0	3.112076	-0.714595	-0.519005
5	1	0	1.836787	-1.707446	0.262612
6	1	0	0.820026	1.932176	1.389375
7	1	0	2.498243	1.358783	1.205648
8	1	0	1.256650	0.295541	1.948610
9	14	0	-1.207445	-0.545950	-0.577945
10	6	0	-2.102599	1.162504	-0.400465
11	1	0	-1.937561	1.806143	-1.271130
12	1	0	-3.180196	0.950656	-0.373453
13	1	0	-1.872938	1.735743	0.505981
14	6	0	-1.299269	-1.156786	1.259049
15	1	0	-2.311068	-1.561967	1.400663
16	1	0	-0.614517	-1.987781	1.464609
17	1	0	-1.159182	-0.388163	2.028741
18	16	0	0.996582	0.446916	-0.464864

$SiMe_2$+Me_2S complex (anti)

E(ZPE)=	0.147457	E(Thermal)=	0.158821
E(CCSD(T))=	-845.683859	E(Empiric)=	-0.131993
DE(Plus)=	-0.015193	DE(2DF)=	-0.279083
E(Delta-G3XP)=	-0.899244	DE(HF)=	-0.032869
G4(0 K)=	-846.894783	G4 Energy=	-846.883419
G4 Enthalpy=	-846.882475	G4 Free Energy=	-846.931522

Number	Atomic #	Type	X	Y	Z
1	6	0	1.852358	-1.393174	0.227749
2	6	0	1.852358	1.393174	0.227749
3	1	0	1.704990	-1.348690	1.308977
4	1	0	1.405091	-2.306619	-0.166772
5	1	0	2.912572	-1.364441	-0.030189
6	1	0	1.405090	2.306619	-0.166772
7	1	0	2.912572	1.364441	-0.030190
8	1	0	1.704989	1.348690	1.308977
9	14	0	-1.112782	0.000000	0.732231
10	6	0	-1.856472	-1.472325	-0.285820
11	1	0	-1.393757	-2.434570	-0.038796
12	1	0	-2.909203	-1.557343	0.019104
13	1	0	-1.850020	-1.349836	-1.375094
14	6	0	-1.856472	1.472325	-0.285820
15	1	0	-2.909203	1.557343	0.019104
16	1	0	-1.393756	2.434570	-0.038796
17	1	0	-1.850020	1.349836	-1.375094
18	16	0	0.993060	0.000000	-0.561802

$SiMe_2$ + Me_2NH Complex

E(ZPE)=	0.165963	E(Thermal)=	0.176025
E(CCSD(T))=	-503.246729	E(Empiric)=	-0.131993
DE(Plus)=	-0.016926	DE(2DF)=	-0.266230
E(Delta-G3XP)=	-0.624842	DE(HF)=	-0.028993
G4(0 K)=	-504.149750	G4 Energy=	-504.139688
G4 Enthalpy=	-504.138744	G4 Free Energy=	-504.183737

Number	Atomic #	Type	X	Y	Z
1	7	0	-0.973800	-0.000034	0.290614
2	6	0	-1.760118	-1.221101	0.009044
3	6	0	-1.759802	1.221358	0.009583
4	1	0	-1.931019	-1.279412	-1.068396
5	1	0	-1.190330	-2.096192	0.321415
6	1	0	-2.721841	-1.200603	0.533886
7	1	0	-1.190560	2.096062	0.324001
8	1	0	-2.722309	1.200082	0.532954
9	1	0	-1.929141	1.281138	-1.068040
10	14	0	0.822286	-0.000157	-0.731686
11	6	0	1.537663	-1.457084	0.334555
12	1	0	1.185472	-2.444028	0.013388
13	1	0	2.625382	-1.462949	0.182730
14	1	0	1.379183	-1.373951	1.420639
15	6	0	1.537837	1.457094	0.334020
16	1	0	2.625562	1.462675	0.182361
17	1	0	1.185664	2.443864	0.012374
18	1	0	1.379207	1.374441	1.420137
19	1	0	-0.724150	-0.000292	1.278641

$SiMe_2$ + Me_3N Complex

E(ZPE)=	0.193352	E(Thermal)=	0.204583
E(CCSD(T))=	-542.422140	E(Empiric)=	-0.152834
DE(Plus)=	-0.019606	DE(2DF)=	-0.305594
E(Delta-G3XP)=	-0.682083	DE(HF)=	-0.032479
G4(0 K)=	-543.421384	G4 Energy=	-543.410152
G4 Enthalpy=	-543.409208	G4 Free Energy=	-543.456701

Number	Atomic #	Type	X	Y	Z
1	7	0	0.951767	-0.000032	0.027137
2	6	0	1.032592	-0.000431	1.502953
3	6	0	1.623059	1.206014	-0.507711
4	6	0	1.622847	-1.205997	-0.508267
5	1	0	0.534158	0.886950	1.893763
6	1	0	2.079943	-0.000586	1.833889
7	1	0	0.534013	-0.887912	1.893339
8	1	0	1.519266	1.215295	-1.594250
9	1	0	1.143478	2.097228	-0.100993
10	1	0	2.685854	1.208106	-0.232787
11	1	0	1.142438	-2.097307	-0.102718
12	1	0	2.685412	-1.208888	-0.232466
13	1	0	1.519870	-1.214257	-1.594874
14	14	0	-1.026522	0.000031	-0.792887
15	6	0	-1.702020	1.464610	0.281627
16	1	0	-1.285713	2.438821	0.000286
17	1	0	-2.775159	1.525686	0.050850
18	1	0	-1.627550	1.356905	1.371677
19	6	0	-1.702579	-1.464225	0.281681
20	1	0	-2.775715	-1.524944	0.050837
21	1	0	-1.286622	-2.438647	0.000485
22	1	0	-1.628125	-1.356486	1.371723

$SiMe_2$ + Me_2PH Complex

E(ZPE)=	0.155866	E(Thermal)=	0.167395
E(CCSD(T))=	-789.469664	E(Empiric)=	-0.131993
DE(Plus)=	-0.015298	DE(2DF)=	-0.277070
E(Delta-G3XP)=	-0.890157	DE(HF)=	-0.032184
G4(0 K)=	-790.660500	G4 Energy=	-790.648972
G4 Enthalpy=	-790.648027	G4 Free Energy=	-790.697188

Number	Atomic #	Type	X	Y	Z
1	15	0	0.949167	-0.000003	0.357361
2	6	0	1.938541	1.457128	-0.160957
3	6	0	1.938554	-1.457119	-0.160977
4	1	0	1.927110	1.514562	-1.251745
5	1	0	1.476734	2.364094	0.236770
6	1	0	2.969454	1.391162	0.194405
7	1	0	1.476756	-2.364094	0.236739
8	1	0	2.969467	-1.391148	0.194385
9	1	0	1.927122	-1.514540	-1.251765
10	14	0	-1.150854	-0.000006	-0.696746
11	6	0	-1.900507	1.497979	0.287348
12	1	0	-1.394658	2.441873	0.054712
13	1	0	-2.937080	1.618643	-0.053162
14	1	0	-1.933641	1.380495	1.376478
15	6	0	-1.900513	-1.497974	0.287368
16	1	0	-2.937086	-1.618638	-0.053140

17	1	0	-1.394668	-2.441873	0.054744
18	1	0	-1.933646	-1.380477	1.376496
19	1	0	1.202133	-0.000010	1.762426

$SiMe_2$ + Me_3P Complex

E(ZPE)=	0.184069	E(Thermal)=	0.197345
E(CCSD(T))=	-828.665868	E(Empiric)=	-0.152834
DE(Plus)=	-0.017497	DE(2DF)=	-0.316684
E(Delta-G3XP)=	-0.949468	DE(HF)=	-0.035977
G4(0 K)=	-829.954258	G4 Energy=	-829.940982
G4 Enthalpy=	-829.940038	G4 Free Energy=	-829.992893

Number	Atomic #	Type	X	Y	Z
1	15	0	0.821403	-0.000003	-0.014241
2	6	0	1.278537	0.000002	1.774416
3	6	0	1.727958	1.447658	-0.683556
4	6	0	1.727973	-1.447654	-0.683554
5	1	0	0.851587	0.885033	2.252910
6	1	0	2.362926	0.000013	1.922567
7	1	0	0.851605	-0.885038	2.252910
8	1	0	1.588506	1.482798	-1.766320
9	1	0	1.311977	2.363310	-0.255321
10	1	0	2.795628	1.396470	-0.452543
11	1	0	1.312005	-2.363311	-0.255315
12	1	0	2.795643	-1.396453	-0.452543
13	1	0	1.588520	-1.482800	-1.766318
14	14	0	-1.403352	-0.000002	-0.775413
15	6	0	-1.977714	1.498299	0.329522
16	1	0	-1.520072	2.442836	0.012816
17	1	0	-3.057295	1.619630	0.172756
18	1	0	-1.825961	1.386804	1.410067
19	6	0	-1.977725	-1.498298	0.329522
20	1	0	-3.057306	-1.619622	0.172754
21	1	0	-1.520088	-2.442837	0.012816
22	1	0	-1.825972	-1.386803	1.410067

Dimethylgermylene ($GeMe_2$)

E(ZPE)=	0.069050	E(Thermal)=	0.074999
E(CCSD(T))=	-2154.821913	E(Empiric)=	-0.062523
DE(Plus)=	-0.006765	DE(2DF)=	-0.121856
E(Delta-G3XP)=	-1.221412	DE(HF)=	-0.069881
G4(0 K)=	-2156.235300	G4 Energy=	-2156.229351
G4 Enthalpy=	-2156.228407	G4 Free Energy=	-2156.264235

Number	Atomic #	Type	X	Y	Z
1	32	0	0.000000	0.000000	0.515852
2	6	0	0.000000	1.491434	-0.827141
3	6	0	0.000000	-1.491434	-0.827141
4	1	0	1.025785	1.561952	-1.219361
5	1	0	-0.255367	2.458569	-0.388135
6	1	0	-0.653156	1.290992	-1.683287
7	1	0	0.255367	-2.458569	-0.388135
8	1	0	0.653156	-1.290992	-1.683287
9	1	0	-1.025785	-1.561952	-1.219361

$GeMe_2$+MeOH Complex

E(ZPE)=	0.122491	E(Thermal)=	0.132612
E(CCSD(T))=	-2270.219978	E(Empiric)=	-0.111152
DE(Plus)=	-0.016400	DE(2DF)=	-0.235501
E(Delta-G3XP)=	-1.362118	DE(HF)=	-0.082638
G4(0 K)=	-2271.905295	G4 Energy=	-2271.895174
G4 Enthalpy=	-2271.894230	G4 Free Energy=	-2271.941715

Number	Atomic #	Type	X	Y	Z
1	6	0	2.615783	-0.080594	-0.050511
2	1	0	2.664615	-0.441721	-1.077742
3	1	0	2.641092	1.013599	-0.050002
4	8	0	1.381537	-0.574913	0.492523
5	32	0	-0.518346	0.030824	-0.551683
6	6	0	-1.544043	-1.216520	0.662129
7	1	0	-2.610551	-0.985115	0.538657
8	1	0	-1.404693	-2.262429	0.374241
9	1	0	-1.311089	-1.105993	1.727399
10	6	0	-0.607693	1.658966	0.660489
11	1	0	-0.490733	1.436639	1.729284
12	1	0	0.118716	2.427486	0.376446
13	1	0	-1.603409	2.105658	0.538566
14	1	0	3.460114	-0.477361	0.521441
15	1	0	1.286440	-0.268944	1.402733

$GeMe_2$+Me_2O Complex (gauche)

E(ZPE)=	0.150310	E(Thermal)=	0.161658
E(CCSD(T))=	-2309.393408	E(Empiric)=	-0.131993
DE(Plus)=	-0.018169	DE(2DF)=	-0.272030
E(Delta-G3XP)=	-1.419438	DE(HF)=	-0.086052
G4(0 K)=	-2311.170778	G4 Energy=	-2311.159430
G4 Enthalpy=	-2311.158486	G4 Free Energy=	-2311.208175

Number	Atomic #	Type	X	Y	Z
1	6	0	-1.822764	1.173964	0.705150
2	6	0	-2.313171	-0.815495	-0.501136
3	1	0	-1.037862	1.921190	0.815259
4	1	0	-2.733923	1.649990	0.322785
5	1	0	-1.857266	-1.491419	-1.224587
6	1	0	-2.564664	-1.366743	0.413768
7	8	0	-1.355772	0.205814	-0.229664
8	32	0	0.819822	-0.449827	-0.344761
9	6	0	1.446035	1.453868	-0.605529
10	1	0	2.543952	1.413692	-0.632063
11	1	0	1.119495	1.859925	-1.567500
12	1	0	1.171025	2.152588	0.192157
13	6	0	1.013780	-0.502600	1.671079
14	1	0	0.721463	0.418599	2.186044
15	1	0	0.480160	-1.347652	2.117513
16	1	0	2.082223	-0.660740	1.872974
17	1	0	-2.032939	0.709652	1.676338
18	1	0	-3.223078	-0.369564	-0.920387

$GeMe_2$+Me_2O Complex (anti)

E(ZPE)=	0.150521	E(Thermal)=	0.161778
E(CCSD(T))=	-2309.394122	E(Empiric)=	-0.131993
DE(Plus)=	-0.018505	DE(2DF)=	-0.272264
E(Delta-G3XP)=	-1.419020	DE(HF)=	-0.085919
G4(0 K)=	-2311.171303	G4 Energy=	-2311.160046
G4 Enthalpy=	-2311.159102	G4 Free Energy=	-2311.208547

Number	Atomic #	Type	X	Y	Z
1	6	0	2.082441	1.185547	0.054433
2	6	0	2.082390	-1.185557	0.054383
3	1	0	1.459272	2.031176	0.343423
4	1	0	3.012513	1.194857	0.634765
5	1	0	1.459184	-2.031167	0.343363
6	1	0	2.314248	-1.243927	-1.016240
7	8	0	1.345125	0.000003	0.348748
8	32	0	-0.771794	-0.000013	-0.542667
9	6	0	-1.318986	-1.498952	0.700738
10	1	0	-2.417424	-1.505089	0.715550
11	1	0	-1.001980	-2.485300	0.348287
12	1	0	-0.978974	-1.355621	1.731412
13	6	0	-1.318995	1.499015	0.700646
14	1	0	-0.978328	1.356043	1.731156
15	1	0	-1.002589	2.485410	0.347793
16	1	0	-2.417423	1.504683	0.716123
17	1	0	2.314332	1.243939	-1.016184
18	1	0	3.012471	-1.194927	0.634700

$GeMe_2$+Me_2S Complex (gauche)

E(ZPE)=	0.146213	E(Thermal)=	0.158108
E(CCSD(T))=	-2632.020452	E(Empiric)=	-0.131993
DE(Plus)=	-0.013682	DE(2DF)=	-0.274958
E(Delta-G3XP)=	-1.684696	DE(HF)=	-0.087195
G4(0 K)=	-2634.066762	G4 Energy=	-2634.054868
G4 Enthalpy=	-2634.053924	G4 Free Energy=	-2634.104956

Number	Atomic #	Type	X	Y	Z
1	6	0	-1.897039	1.316621	0.859681
2	6	0	-2.259054	-1.218088	-0.253869
3	1	0	-1.366343	2.268083	0.802072
4	1	0	-2.973043	1.496071	0.808465
5	1	0	-1.982763	-1.908211	-1.051835
6	1	0	-1.959134	-1.637340	0.708453
7	32	0	1.070623	-0.470943	-0.292608
8	6	0	1.782676	1.418163	-0.504873
9	1	0	2.866798	1.360968	-0.343710
10	1	0	1.629234	1.797607	-1.519469
11	1	0	1.386690	2.144448	0.212563
12	6	0	1.010817	-0.503211	1.740025
13	1	0	0.749070	0.448358	2.213993
14	1	0	0.354659	-1.290395	2.126558
15	1	0	2.027599	-0.758735	2.066652
16	1	0	-1.635695	0.808610	1.789065
17	1	0	-3.335556	-1.037415	-0.275625
18	16	0	-1.365365	0.331075	-0.576218

$GeMe_2$+Me_2S Complex (anti)

E(ZPE)=	0.146052	E(Thermal)=	0.158080
E(CCSD(T))=	-2632.021343	E(Empiric)=	-0.131993
DE(Plus)=	-0.013951	DE(2DF)=	-0.275153
E(Delta-G3XP)=	-1.684357	DE(HF)=	-0.087192
G4(0 K)=	-2634.067936	G4 Energy=	-2634.055908
G4 Enthalpy=	-2634.054964	G4 Free Energy=	-2634.106892

Number	Atomic #	Type	X	Y	Z
1	6	0	2.134110	1.396401	-0.216428
2	6	0	2.140885	-1.392783	-0.225618
3	1	0	1.689682	2.304909	0.192713
4	1	0	3.208025	1.394650	-0.020141
5	1	0	1.700274	-2.306171	0.176816
6	1	0	1.938621	-1.330929	-1.296898
7	32	0	-0.955058	-0.002586	-0.549830
8	6	0	-1.633246	-1.514949	0.624900
9	1	0	-2.709867	-1.600800	0.427986
10	1	0	-1.186832	-2.479042	0.360989
11	1	0	-1.508429	-1.343851	1.698512
12	6	0	-1.623346	1.524266	0.612013
13	1	0	-1.495669	1.363455	1.686889
14	1	0	-1.174422	2.484091	0.336995
15	1	0	-2.700348	1.611946	0.418018
16	1	0	1.931604	1.341194	-1.288053
17	1	0	3.214668	-1.387709	-0.028592
18	16	0	1.346509	-0.002913	0.635008

$GeMe_2$+Me_2NH Complex

E(ZPE)=	0.164319	E(Thermal)=	0.175097
E(CCSD(T))=	-2289.579417	E(Empiric)=	-0.131993
DE(Plus)=	-0.015936	DE(2DF)=	-0.265644
E(Delta-G3XP)=	-1.407522	DE(HF)=	-0.083478
G4(0 K)=	-2291.319670	G4 Energy=	-2291.308892
G4 Enthalpy=	-2291.307948	G4 Free Energy=	-2291.355772

Number	Atomic #	Type	X	Y	Z
1	7	0	-1.287297	-0.000030	0.381353
2	6	0	-2.034854	-1.222554	0.039002
3	6	0	-2.034785	1.222556	0.039083
4	1	0	-2.137613	-1.275059	-1.047813
5	1	0	-1.474761	-2.094536	0.378412
6	1	0	-3.032404	-1.226818	0.495903
7	1	0	-1.474622	2.094483	0.378527
8	1	0	-3.032325	1.226864	0.496007
9	1	0	-2.137558	1.275121	-1.047726
10	32	0	0.713792	-0.000027	-0.549529
11	6	0	1.333314	-1.506867	0.670587
12	1	0	0.982413	-2.490453	0.341269
13	1	0	2.428875	-1.530365	0.613952
14	1	0	1.073428	-1.376857	1.729032
15	6	0	1.333187	1.506975	0.670449
16	1	0	2.428745	1.530572	0.613795
17	1	0	0.982183	2.490500	0.341057
18	1	0	1.073327	1.377026	1.728908
19	1	0	-1.091136	-0.000061	1.379394

$GeMe_2$+Me_3N Complex

E(ZPE)=	0.191464	E(Thermal)=	0.203488
E(CCSD(T))=	-2328.756201	E(Empiric)=	-0.152834
DE(Plus)=	-0.018553	DE(2DF)=	-0.305039
E(Delta-G3XP)=	-1.465181	DE(HF)=	-0.086853
G4(0 K)=	-2330.593198	G4 Energy=	-2330.581174
G4 Enthalpy=	-2330.580229	G4 Free Energy=	-2330.630713

Number	Atomic #	Type	X	Y	Z
1	7	0	1.258966	-0.000029	0.068921
2	6	0	1.469259	-0.000576	1.526883
3	6	0	1.858992	1.207027	-0.530619
4	6	0	1.859047	-1.206616	-0.531517
5	1	0	1.006895	0.886303	1.961757
6	1	0	2.542169	-0.000309	1.768549
7	1	0	1.007522	-0.888153	1.960997
8	1	0	1.662225	1.208762	-1.604557
9	1	0	1.404928	2.095753	-0.089029
10	1	0	2.943944	1.232293	-0.356307
11	1	0	1.404597	-2.095693	-0.091023
12	1	0	2.943913	-1.232254	-0.356717
13	1	0	1.662784	-1.207264	-1.605544
14	32	0	-0.917986	-0.000004	-0.571632
15	6	0	-1.456299	1.513970	0.672458
16	1	0	-1.044805	2.482163	0.368346
17	1	0	-2.547128	1.599300	0.579070
18	1	0	-1.238862	1.351575	1.734029
19	6	0	-1.456562	-1.513793	0.672538
20	1	0	-2.547470	-1.598450	0.579359
21	1	0	-1.045712	-2.482218	0.368311
22	1	0	-1.238839	-1.351556	1.734072

$GeMe_2$+Me_2PH Complex

E(ZPE)=	0.154586	E(Thermal)=	0.166699
E(CCSD(T))=	-2575.805046	E(Empiric)=	-0.131993
DE(Plus)=	-0.014259	DE(2DF)=	-0.273976
E(Delta-G3XP)=	-1.674305	DE(HF)=	-0.086471
G4(0 K)=	-2577.831465	G4 Energy=	-2577.819352
G4 Enthalpy=	-2577.818408	G4 Free Energy=	-2577.869945

Number	Atomic #	Type	X	Y	Z
1	15	0	0.656656	1.176525	0.000000
2	6	0	0.298927	2.241964	1.453946
3	6	0	0.298927	2.241964	-1.453946
4	1	0	-0.780101	2.406265	1.507551
5	1	0	0.611275	1.722783	2.363246
6	1	0	0.811985	3.204622	1.392145
7	1	0	0.611275	1.722783	-2.363246
8	1	0	0.811985	3.204622	-1.392145
9	1	0	-0.780101	2.406265	-1.507551
10	32	0	-0.724376	-0.875883	0.000000
11	6	0	0.298927	-1.734164	1.539222
12	1	0	0.132673	-1.208976	2.485200
13	1	0	-0.113059	-2.742968	1.660862
14	1	0	1.375556	-1.835643	1.371950
15	6	0	0.298927	-1.734164	-1.539222
16	1	0	-0.113059	-2.742968	-1.660862

17	1	0	0.132673	-1.208976	-2.485200
18	1	0	1.375556	-1.835643	-1.371950
19	1	0	2.079282	1.194610	0.000000

$GeMe_2$+Me_3P Complex

E(ZPE)=	0.182583	E(Thermal)=	0.196534
E(CCSD(T))=	-2615.000942	E(Empiric)=	-0.152834
DE(Plus)=	-0.016560	DE(2DF)=	-0.314134
E(Delta-G3XP)=	-1.733520	DE(HF)=	-0.090280
G4(0 K)=	-2617.125687	G4 Energy=	-2617.111737
G4 Enthalpy=	-2617.110793	G4 Free Energy=	-2617.166631

Number	Atomic #	Type	X	Y	Z
1	15	0	-1.156343	0.000000	0.021239
2	6	0	-1.758410	0.000000	1.763658
3	6	0	-2.009870	-1.445555	-0.722277
4	6	0	-2.009870	1.445555	-0.722277
5	1	0	-1.373450	-0.884981	2.276427
6	1	0	-2.851594	0.000000	1.818044
7	1	0	-1.373450	0.884981	2.276427
8	1	0	-1.794481	-1.474141	-1.793005
9	1	0	-1.621032	-2.362796	-0.272513
10	1	0	-3.092157	-1.401625	-0.569611
11	1	0	-1.621032	2.362797	-0.272513
12	1	0	-3.092157	1.401625	-0.569611
13	1	0	-1.794481	1.474141	-1.793005
14	32	0	1.243965	0.000000	-0.551566
15	6	0	1.671954	-1.540300	0.719851
16	1	0	1.233198	-2.484262	0.379654
17	1	0	2.760044	-1.671988	0.696184
18	1	0	1.385538	-1.371444	1.763179
19	6	0	1.671954	1.540300	0.719851
20	1	0	2.760044	1.671988	0.696184
21	1	0	1.233198	2.484262	0.379654
22	1	0	1.385538	1.371444	1.763179

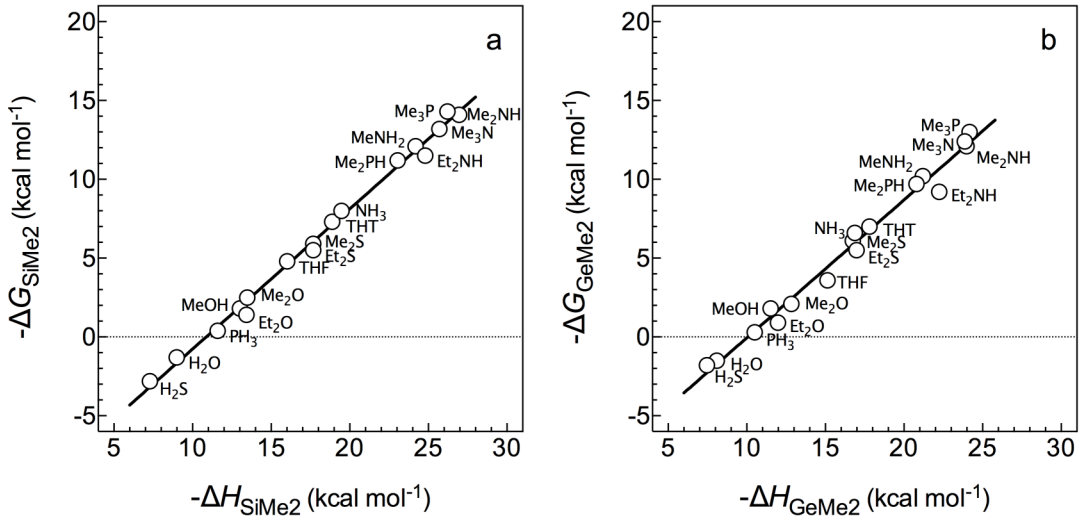

Figure S29. Plots of calculated Δ*G* vs. Δ*H* values for the complexation of (a) $SiMe_2$ and (b) $GeMe_2$ with chalcogen and pnictogen donors (standard state: gas phase at 1 atm, 298.15K).

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