

Supplementary Information

Organogermanium Reactive Intermediates. The Direct Detection and Characterization of Transient Germylenes and Digermenes in Solution.

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Figure 1. *Lower:* Partial 600 MHz ^1H NMR spectrum of product mixture from 248 nm laser-drop photolysis of **4a** in deoxygenated hexane containing 0.003 M MeOH. *Middle:* Lower spectrum spiked with authentic **12**. *Upper:* Middle spectrum spiked with authentic **9a**. The labeled peaks are due to impurities.

Figure 2. Quantum yield determination for the extrusion of Ph_2Ge (trapped by MeOH as **9a**) from **4a**, standardized against methoxymethyldiphenylsilane (**14**, from reaction of MeOH with diphenylsilene, $\Phi = 0.21 \pm 0.02$ from photolysis of **13**¹³).

Figure 3. Determination of molar absorptivity of Ph_2Ge at 500 nm, using the benzophenone triplet at 525 nm in dry, deoxygenated hexane ($\epsilon_{525} = 6250 \pm 1250$)¹⁴ as actinometer. Plots of $\Delta A_{\text{max},\lambda}$ vs. laser dose for optically matched deoxygenated solutions of benzophenone and **4a** in dry hexane, excited at 248 nm.

Table 1. Structure optimization of **20**.

Table 2. Comparison of XC functional and basis-sets for the calculation of the energies and oscillator strengths of the first 10 allowed transitions of **20** under C_2 symmetry.

Table 3. Ge-centered molecular dimensions of optimized germylenes.

Table 4. Calculated energies and oscillator strengths (f) of the first 10 allowed transitions of germylenes under C_2 symmetry.

Table 5. Optimized Ge-centered molecular dimensions of digermenes $\text{R}_2\text{Ge}=\text{GeR}_2$.

Table 6. Calculated energies and oscillator strengths of the first 10 allowed transitions of digermenes $\text{R}_2\text{Ge}=\text{GeR}_2$.

Synthesis and Characterization of Compounds

Figure 1. Lower: Partial 600 MHz ^1H NMR spectrum of product mixture from 248 nm laser-drop photolysis of **4a** in deoxygenated hexane containing 0.003 M MeOH. Middle: Lower spectrum spiked with authentic **12**. Upper: Middle spectrum spiked with authentic **9a**. The labeled peaks are due to impurities.

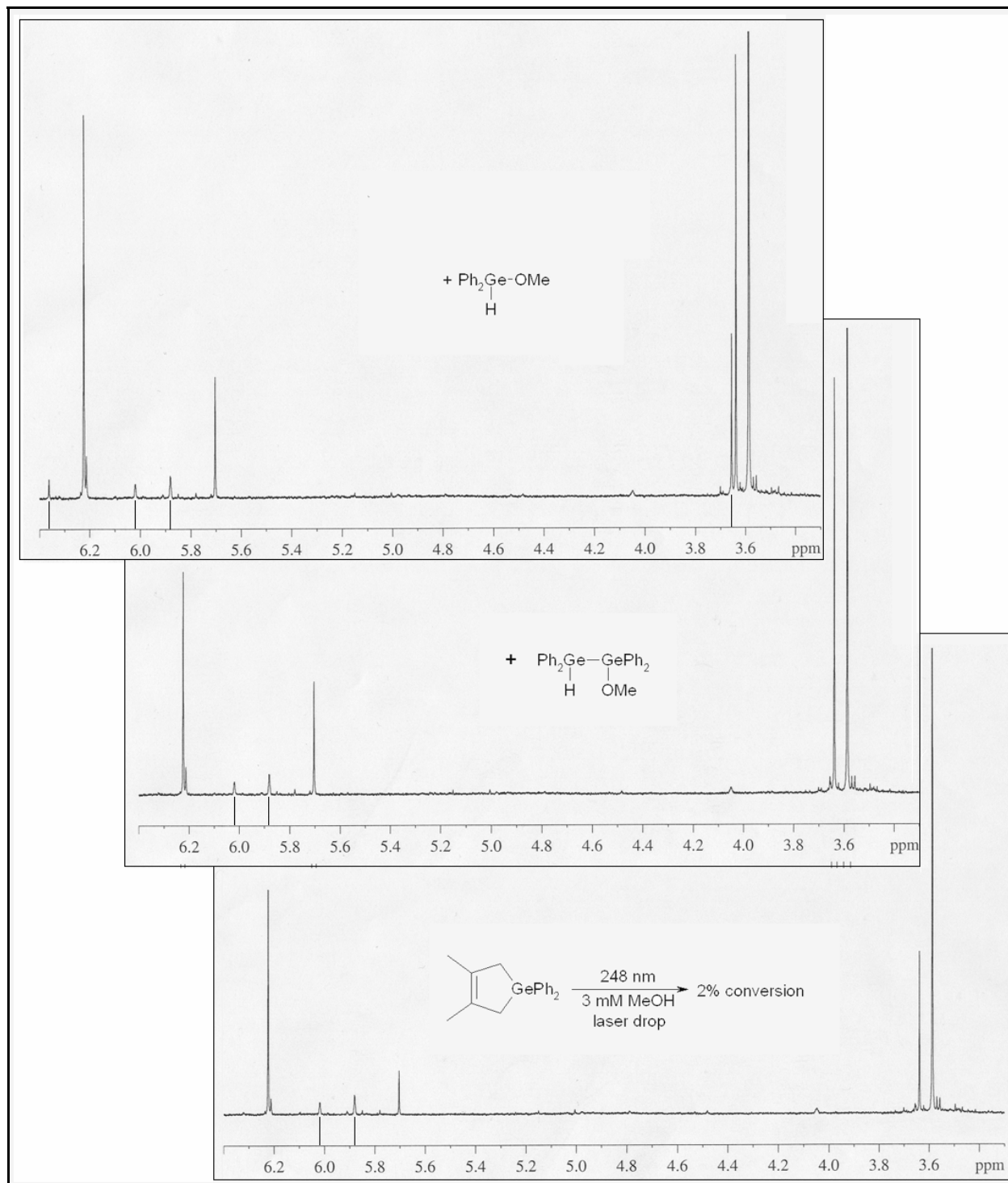


Figure 2. Quantum yield determination for the extrusion of Ph_2Ge (trapped as **9a**) from photolysis of **4a** (0.037 M) in cyclohexane- d_{12} containing 0.5 M MeOH, using the formation of methoxy-methyldiphenylsilane (**14**) from photolysis of **13** (0.043 M) in the same hexane/MeOH mixture as actinometer ($\Phi_{14} = 0.21 \pm 0.02^{13}$). The peak due to residual $\text{C}_6\text{D}_{11}\text{H}$ was used as internal standard. “% Conversion” is defined as the ratio $[\text{product}]/([\text{starting material}] + [\text{product}]) \times 100\%$.

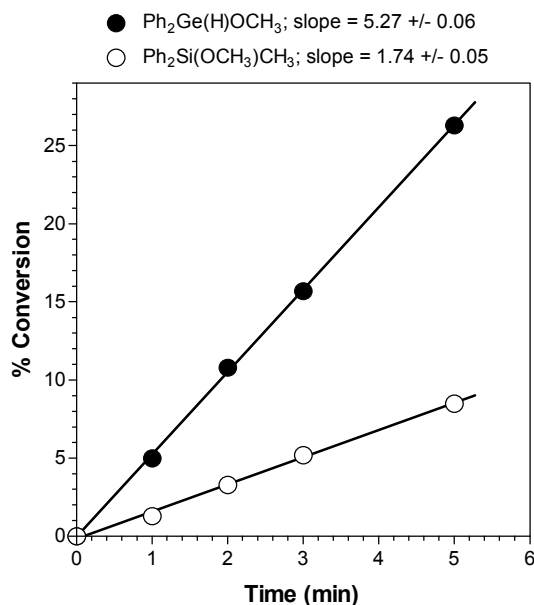


Figure 3. Determination of molar absorptivity of Ph_2Ge at 500 nm, using the benzophenone triplet at 525 nm in dry, deoxygenated hexane ($\epsilon_{525} = 6250 \pm 1250$)¹⁴ as actinometer. Plot of $\Delta A_{\text{max},\lambda}$ vs. laser dose for optically matched, flowed, deoxygenated solutions of benzophenone and **4a** in dry hexane, excited at 248 nm.

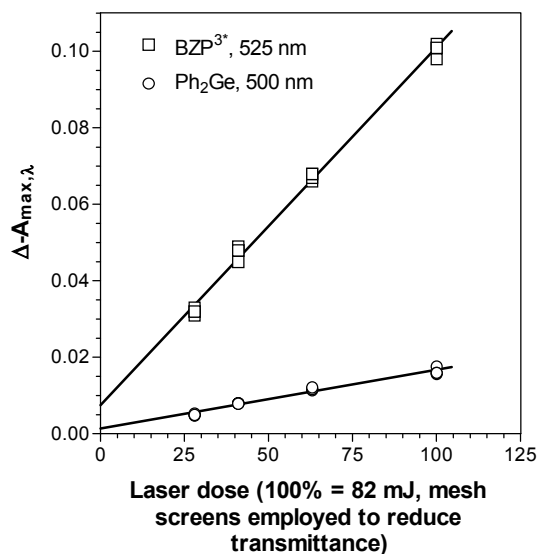
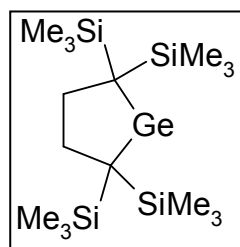


Table 1. Structure optimization of **20**

Method	Experimental	DFT			
	XRDa ¹⁵	RPBE	revPBE	BLYP	PW91
Distances (Å)					
Ge-C	2.010(2) 2.020(2)	2.055	2.054	2.058	2.039
C1-C2	1.562(3) 1.560(3)	1.574	1.573	1.576	1.563
C2-C2	1.529(3)	1.553	1.551	1.554	1.543
C1-Si1	1.905(2) 1.899(2)	1.942	1.941	1.942	1.923
C1-Si2	1.890(2) 1.894(2)	1.945	1.944	1.945	1.925
Angles (°)					
C1-GeC1	90.97(9)	91.40	91.40	91.60	91.00
Ge-C1-C2	105.30(10) 105.50(10)	104.90	104.90	104.70	105.30
C1-C2-C2	111.00(20) 110.30(20)	111.80	111.80	112.00	111.50
Si-C1-Si	111.40 111.30	110.50	110.40	110.70	110.00

PW91 : the exchange and correlation corrections proposed in 1991 by Perdew-Wang.

BLYP : the gradient correction proposed in 1988 by Becke and the Lee-Yang-Parr 1988 correlation correction LYP.

revPBE : the revised PBE exchange correction proposed in 1998 by Zhang-Wang and the correlation term presented in 1996 by Perdew-Burke-Ernzerhof.

RPBE: the revised PBE exchange correction proposed in 1999 by Hammer-Hansen-Norskov and the correlation term presented in 1996 by Perdew-Burke-Ernzerhof.

Table 2. Comparison of XC functional and basis-sets for the calculation of the energies and oscillator strengths (f) of the first 10 allowed transitions of **20** under C_2 symmetry. The lowest energy transition of B symmetry is the n,p transition.

Functional and Basis Set																	
	EXP		BLYP_TZ2P			RPBE_TZ2PE			revPBE			PW91_TZ2P			SAOP_DZP		
	ΔE (eV)	λ_{\max} (nm)	ΔE (eV)	λ_{\max} (nm)	f	ΔE (eV)	λ_{\max} (nm)	f	ΔE (eV)	λ_{\max} (nm)	f	ΔE (eV)	λ_{\max} (nm)	f	ΔE (eV)	λ_{\max} (nm)	f
1A			3.13	396	9.89E-05	3.25	382	1.21E-04	3.24	383	0.0001	3.20	388	1.22E-04	3.32	374	1.03E-04
2A			3.95	314	2.95E-03	4.05	306	3.04E-03	4.03	308	3.15E-03	3.99	311	3.14E-03	4.13	300	3.31E-03
3A			4.22	294	3.31E-06	4.29	289	1.78E-02	4.30	288	1.15E-04	4.28	290	1.32E-04	4.43	280	1.83E-04
4A			4.22	294	1.62E-02	4.32	287	3.38E-04	4.38	283	3.09E-02	4.31	287	1.92E-02	4.61	269	4.38E-04
5A			4.40	281	4.84E-04	4.50	275	3.76E-04	4.48	276	2.76E-04	4.45	278	3.40E-04	4.78	260	3.87E-03
1B	2.76	450	2.44	507	2.93E-03	2.55	486	3.39E-03	2.53	490	3.23E-03	2.51	494	3.44E-03	2.61	475	2.58E-03
2B	4.43	280	3.56	348	3.08E-02	3.65	340	3.01E-02	3.63	341	3.01E-02	3.58	346	2.81E-02	3.71	334	3.34E-02
3B			4.22	294	1.72E-04	4.32	287	2.47E-04	4.30	288	3.21E-04	4.27	290	6.96E-04	4.42	280	8.85E-04
4B			4.31	288	2.34E-02	4.40	282	2.32E-02	4.38	283	2.46E-02	4.34	285	1.31E-02	4.50	276	1.74E-02
5B			4.39	282	1.40E-02	4.49	276	1.52E-02	4.47	277	1.55E-02	4.44	279	1.46E-02	4.60	270	1.15E-02

Functional and Basis Set																	
	EXP		RPBE_DZP			RPBE_DZP_ZORA			SAOP_TZ2P			SAOP_TZ2P_ZORA			SAOP_QZ4P_ZORA		
	ΔE (eV)	λ_{\max} (nm)	ΔE (eV)	λ_{\max} (nm)	f	ΔE (eV)	λ_{\max} (nm)	f	ΔE (eV)	λ_{\max} (nm)	f	ΔE (eV)	λ_{\max} (nm)	f	ΔE (eV)	λ_{\max} (nm)	f
1A			3.28	378	1.28E-04	3.28	378	1.10E-04	3.35	370	1.02E-04	3.33	372	1.00E-04	3.38	367	8.31E-05
2A			4.07	305	3.11E-03	4.08	304	2.70E-03	4.18	297	3.59E-03	4.17	298	3.33E-03	4.18	296	3.19E-03
3A			4.33	286	1.82E-04	4.35	285	9.45E-05	4.47	277	1.39E-02	4.50	276	1.43E-03	4.50	276	3.31E-04
4A			4.51	275	2.60E-04	4.53	274	3.41E-04	4.51	275	2.09E-04	4.50	276	1.33E-02	4.50	275	1.16E-02
5A						4.72	263	3.51E-03	4.69	264	4.78E-04	4.69	265	4.16E-04	4.68	265	7.98E-04
1B	2.76	450	2.56	485	2.74E-03	2.58	480	2.34E-03	2.67	465	3.31E-03	2.68	462	2.75E-03	2.70	459	2.25E-03
2B	4.43	280	3.67	338	3.07E-02	3.68	337	3.15E-02	3.74	331	3.06E-02	3.73	332	3.09E-02	3.77	329	3.05E-02
3B			4.33	287	5.00E-04	4.34	286	7.99E-04	4.50	276	7.86E-04	4.49	276	1.04E-03	4.50	275	1.27E-03
4B			4.40	282	1.56E-02	4.42	280	2.43E-02	4.57	271	1.54E-02	4.57	271	1.49E-02	4.56	272	1.55E-02
5B			4.50	276	1.45E-02	4.51	275	1.42E-02	4.67	266	1.17E-02	4.66	266	1.14E-02	4.66	266	1.27E-02

Table 3. Ge-centered molecular dimensions of optimized germylenes

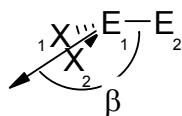
	Bond distance (Å)	Bond angle (°)
	Ge-H	H-Ge-H
H₂Ge	1.606	89.90
	Ge-C	C-Ge-C
Me₂Ge	2.017	97.50
Ph₂Ge	1.993	98.70
Mes₂Ge	2.013	102.80

Table 4. Calculated energies and oscillator strengths (f) of the first 10 allowed transitions of germylenes under C₂ symmetry. The lowest energy transition of B symmetry is the n,p transition.

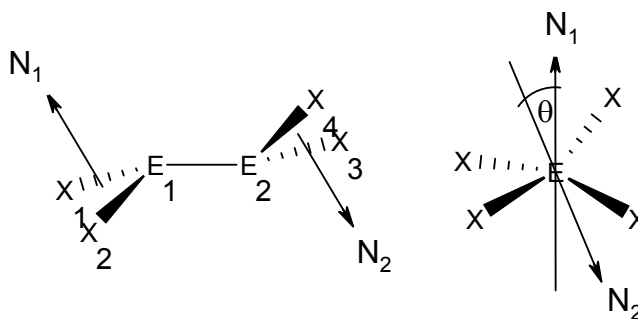
	GeH₂			GeMe₂			GePh₂			GeMes₂		
	ΔE (eV)	λ_{\max} (nm)	f	ΔE (eV)	λ_{\max} (nm)	f	ΔE (eV)	λ_{\max} (nm)	f	ΔE (eV)	λ_{\max} (nm)	f
1A	3.72	333	0.00E+00	3.95	314	1.24E-04	3.31	375	2.19E-03	2.87	432	3.68E-07
2A	6.42	193	2.40E-01	5.39	230	2.98E-02	3.43	362	1.61E-02	2.91	426	1.37E-02
3A	8.23	151	5.00E-03	6.36	195	2.63E-01	3.81	325	6.27E-04	3.68	336	3.54E-04
4A	9.32	133	7.73E-01	6.60	188	6.31E-05	3.85	322	3.78E-03	3.84	323	3.77E-04
5A				7.02		3.15E-02	4.12		3.96E-02	3.93		2.76E-02
1B	2.51	493	7.64E-03	2.68	463	1.40E-02	2.41	514	2.41E-02	2.12	586	3.25E-02
2B	7.16	173	3.55E-02	5.60	221	1.73E-01	3.39	365	3.23E-03	2.92	425	3.50E-03
3B	7.91	157	3.05E-03	6.66	186	4.88E-02	3.52	352	1.26E-01	3.10	400	4.93E-02
4B	8.31	149	3.03E-03	6.79	183	4.44E-02	4.07	305	2.36E-02	3.94	315	6.56E-03
5B	8.67	143	1.10E+00	6.92	179	5.03E-02	4.46	278	1.03E-01	4.22	294	1.00E-01

Table 5. Optimized Ge-centered molecular dimensions of digermenes $R_2Ge=GeR_2$.

	$H_2Ge=GeH_2$	$Me_2Ge=GeMe_2$ 6c	$Ph_2Ge=GePh_2$ 6a	$Mes_2Ge=GeMes_2$ 6b
Distances (Å)				
Ge=Ge	2.293	2.338	2.319	2.278
Ge-R	1.548	1.995	1.971	1.982
	1.549	1.995	1.973	1.980
	1.549	1.995	1.971	1.980
	1.549	1.995	1.970	1.982
Angles (°)				
R-Ge-R	108.20	107.00	111.90	114.40
	108.20	107.00	111.60	114.30
Ge-Ge-R	116.50	117.50	115.10	117.90
	114.70	116.50	117.00	118.50
	114.70	116.50	116.70	118.60
	116.50	117.60	116.00	117.90
Pyramidalization (fold, β)				
	42.55	40.18	38.34	29.28
	42.49	40.24	37.92	29.31
Torsion (θ)				
	1.08	2.85	4.66	7.10



Definition of fold angle



Definition of torsion angle

Table 6. Calculated energies and oscillator strengths (f) of the first 10 allowed transitions of digermenes $R_2Ge=GeR_2$.

	$H_2Ge=GeH_2$			$Me_2Ge=GeMe_2$ 6c			$Ph_2Ge=GePh_2$ 6a			$Mes_2Ge=GeMes_2$ 6b		
	ΔE (eV)	λ_{max} (nm)	f	ΔE (eV)	λ_{max} (nm)	f	ΔE (eV)	λ_{max} (nm)	f	ΔE (eV)	λ_{max} (nm)	f
1	3.57	347	2.15E-01	3.32	374	2.41E-01	2.70	460	2.29E-01	2.66	467	1.92E-01
2	5.33	233	1.03E-01	4.21	294	3.47E-05	3.12	398	3.69E-02	2.85	434	5.11E-02
3	5.71	217	2.08E-03	4.25	292	9.05E-04	3.21	387	3.38E-03	2.92	425	1.53E-02
4	6.98	178	6.76E-02	4.34	285	3.05E-05	3.29	377	1.21E-03	3.06	405	1.63E-02
5	7.08	175	4.17E-02	4.60	270	1.66E-02	3.31	374	2.23E-03	3.14	395	5.63E-06
6	7.15	174	4.21E-01	4.73	262	1.44E-03	3.32	374	2.25E-02	3.21	387	4.02E-03
7	7.40	168	2.98E-02	5.15	241	2.22E-04	3.43	361	2.89E-03	3.27	379	1.32E-05
8	7.58	163	1.13E-03	5.16	240	7.85E-03	3.44	360	5.93E-02	3.40	364	3.38E-02
9	7.97	156	1.77E-01	5.67	219	4.22E-02	3.54	350	3.42E-02	3.48	356	6.13E-02
10	8.30	149	1.36E-01	5.79	214	3.23E-02	3.57	348	5.20E-03	3.55	349	5.22E-02

Synthesis and Characterization of Compounds

^1H , ^{13}C and ^{29}Si NMR spectra were recorded on Bruker AV200, DRX500 or AV600 spectrometers in deuteriochloroform solution unless otherwise noted; ^1H and ^{13}C spectra were referenced to the residual solvent proton and ^{13}C signals, respectively, while ^{29}Si spectra were referenced to an external solution of TMS. Gas chromatographic (GC) separations employed a Hewlett-Packard 5890 Series II gas chromatograph equipped with a HP3396A integrator, a flame ionization detector and a DB-5 column (30m, 0.25 μm ; Chromatographic Specialties, Inc.). Gas chromatographic/mass spectrometric (GC/MS) experiments were carried out on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a HP-5971A mass selective detector and a SPB-5 capillary column (25 m, 0.25 μm ; Supelco, Inc.). High-resolution electron impact mass spectra and exact masses were determined by on a Micromass ToFSpec 2E (MALDI-TOF Mass Spectrometer). Radial chromatographic separations were carried out using a Chromatotron[®] (Harrison Research, Inc.), with silica gel 60 plates (4 mm thick) and using hexane as the eluant. Column chromatography was carried out using a 30 mm x 600 mm column using Silica Gel (~100 g, acid washed, 230-400 mesh) (Silicycle). Steady state photolyses were carried out in a Rayonet[®] photochemical reactor (Southern New England Ultraviolet Co.) equipped with a merry-go-round apparatus and 6 RPR-2537 lamps (254 nm) or a 16W Philips 93106E zinc resonance lamp (214 nm). Melting points were determined using a Mettler FP82 hot stage mounted on a polarizing microscope and are uncorrected.

Germanium tetrachloride and 1,1,3,3-tetramethyldisiloxane were used as received from Gelest Inc., as were 2,3-dimethyl-1,3-butadiene, phenylmagnesium bromide (3 M solution in ether), chlorotriethylsilane, *tert*-butyllithium (1.7M in pentane), 2-bromo-1,3,5-trimethylbenzene, and magnesium (all from Sigma-Aldrich). Diethyl ether (Caledon Reagent)

and tetrahydrofuran (Caledon Reagent) were dried by passage through activated alumina under nitrogen using a Solv-Tec solvent purification system (Solv-Tec, Inc.). Hexanes (EMD OmniSolv) was refluxed for several days over sodium / potassium amalgam under nitrogen and distilled. *n*-Butylamine (Sigma-Aldrich) was distilled from solid KOH. Triethylsilane (Sigma-Aldrich) was purified by distillation from lithium aluminum hydride. Isoprene (Sigma-Aldrich) was purified by passage through activated alumina. Methanol (Aldrich Spectroscopic grade) was refluxed over magnesium/iodine and distilled prior to use. Glacial acetic acid was used as received from Caledon Laboratories.

Germanium dichloride-dioxane and 1,1-dichloro-3,4-dimethyl-2,5-dihydro-1H-germole (**7**) were prepared by modifications of the procedures of Nefedov and coworkers.^{1,2} For the former, a mixture of germanium tetrachloride (25.0 g, 0.117 mol), 1,1,3,3-tetramethyldisiloxane (17.3 g, 0.129 mol) and 1,4-dioxane (18.0 g, 0.205 mol) were combined in a flame-dried 100 mL round-bottom flask equipped with a reflux condenser and nitrogen inlet, heated to 85° C over 1 h, and then left at this temperature for a further 12 h. The resulting suspension of colorless crystals was cooled and the excess solution was decanted off. The crystals were washed with pentane (5 x 20 mL), and then pumped on under vacuum for 1 h to yield GeCl₂-dioxane as colorless needles (21.9 g, 0.095 mol, 81%, mp 100-150 °C¹). For the preparation of **7**, GeCl₂-dioxane (5.0 g, 0.0216 mol) and dry THF (100 mL) were combined in a flame-dried two-necked round-bottom 250 mL flask fitted with reflux condenser, addition funnel, nitrogen inlet, and magnetic stirrer. The solution was heated to reflux with stirring under nitrogen, and then a solution of 2,3-dimethyl-1,3-butadiene (2.3 g, 0.028 mol) in dry THF (20 mL) was added dropwise over 1 h. The solution was stirred for a further ten minutes, the apparatus was reconfigured for distillation, and the solvent was distilled off under nitrogen. Continued distillation under vacuum afforded **7**

as a colorless liquid (4.29 g, 0.019 mmol, 88%; 48 °C, 0.2 mm Hg) whose boiling point and ^1H NMR spectrum agreed well with previously reported data.²

3,4-Dimethyl-1,1-diphenyl-2,5-dihydro-1H-germole (4a) was prepared by a modification of the procedure of Manuel and coworkers.³ A solution of **7** (5.00 g, 0.0221 mol) in anhydrous THF (100 mL) was prepared in a flame-dried apparatus consisting of a 250 mL, two-necked round-bottom flask, reflux condenser, addition funnel, and magnetic stirrer. The solution was cooled in a cold water bath (5 °C), and then a solution of phenyl magnesium bromide (18.5 mL of a 3.0 M solution in diethyl ether, 0.0555 mol) in anhydrous THF (25 mL) was added dropwise with stirring over 1 h. The cooling bath was removed and the reaction mixture was allowed to stir at room temperature for 24 h. The resulting yellow solution was hydrolyzed with saturated aqueous ammonium chloride (25 mL) and transferred to a separatory funnel in order to separate the aqueous and organic fractions. The aqueous fraction was extracted with diethyl ether (2 x 75 mL), and then the combined ether fractions were washed with water (1 x 25 mL), 5% aqueous sodium bicarbonate (1 x 25 mL), distilled water (1 x 25 mL), dried with anhydrous magnesium sulfate, and filtered. The solvent was removed on a rotary evaporator to yield a light yellow oil (5.3 g) that solidified upon cooling to -20 °C. The solid was recrystallized slowly, once from 1:1 (v/v) acetone-isopropanol (1:1) and then repeatedly from 1:3 (v/v) acetone-hexane, with GC analysis in between, until < 0.01% biphenyl remained (usually 3 or 4 slow recrystallizations). The product was finally obtained as colorless crystals (4.06 g, 0.0131 mol, 59%; mp 48.6 - 49.3 (lit 40 - 41 °C³)) whose ^1H NMR spectrum agreed well with that previously reported.⁴ ^1H NMR, δ 1.82 (s, 6H), 2.05 (s, 4H), 7.39 (m, 6H), 7.56 (m, 4H); ^{13}C NMR, δ 19.5, 25.7, 128.3, 128.9, 130.9, 134.3, 138.5; MS, m/z = 310 (45), 308 (35), 306 (27), 229 (20), 228 (66), 227 (80), 226

(67), 225 (60), 224 (40), 151 (100), 149 (77), 147 (59), 125 (18), 99 (21); Exact mass: calc. for $C_{18}H_{20}Ge$, 310.0777; found, 310.0774.

3,4-Dimethyl-1,1-bis(2,4,6-trimethylphenyl)-2,5-dihydro-1H-germole (4b) was prepared in similar fashion to **4a**. Magnesium (0.80 g, 0.033 mol) was placed in a 100 mL 2-neck round bottom flask fitted with an addition funnel under dry nitrogen, and the apparatus was flame-dried. A stir bar and anhydrous diethyl ether (20 mL) were added to the vessel, and then 2-bromo-1,3,5-trimethylbenzene (6.17 g, 0.031 mol) was added dropwise through the addition funnel over a 60-minute period. The reaction mixture was stirred for 24 hours, resulting in the formation of a greenish-brown solution. This solution was added to 3.0 g (0.0133 mol) **7** over 30 minutes. The mixture was stirred for 24 hours at 22 °C, and then hydrolyzed with saturated aqueous ammonium chloride (25 mL). The layers were separated and the aqueous fraction was extracted with diethyl ether (2 x 50 mL). The combined organic fractions were washed with water (1 x 25 mL), 5% aqueous sodium bicarbonate (1 x 25 mL), and again with distilled water (1 x 25 mL), dried with anhydrous magnesium sulfate, and filtered. The solvent was removed on a rotary evaporator to yield a pale yellow oil (3.00 g), which was distilled under vacuum to afford **4b** (1.14 g, 0.0029 mol, 22%; 175 °C, 0.08 mm Hg), identified by comparison to previously published data.⁵ Further purification of **4b** by column chromatography (pentane) was performed until the purity of the compound was $\geq 97\%$ according to GC analysis. 1H NMR δ = 1.78 (s, 6H), 2.22 (s, 4H), 2.27 (s, 6H), 2.38 (s, 12H), 6.82 (s, 4H); ^{13}C NMR δ = 19.2, 20.9, 23.9, 32.1, 127.7, 130.8, 137.5, 137.8, 143.2; MS, m/z = 394 (3), 392 (2), 390 (2), 312 (30), 310 (23), 308 (18), 192 (100), 190 (76), 188 (59), 165 (25), 119 (25), 105 (32).

1,1,3,4-Tetramethyl-2,5-dihydro-1H-germole (4c) was prepared in similar fashion to **4a**. To a solution of **7** (4.20 g, 0.0185 mol) in anhydrous THF (75 mL) at 5 °C was added a solution of

methyl magnesium bromide (13.5 mL of a 3.0 M solution in Et₂O, 0.0405 mol) in anhydrous THF (25 mL), and the mixture was stirred at room temperature for 24 h. The reaction was hydrolyzed with saturated aqueous ammonium chloride (25 mL), the layers were separated, and the aqueous fraction was extracted with diethyl ether (2 x 40 mL). The combined organic fractions were washed with water (1 x 25 mL), 5% aqueous sodium bicarbonate (1 x 30 mL), and again with distilled water (1 x 25 mL), dried with anhydrous magnesium sulfate, and filtered. The solvent was removed on a rotary evaporator to yield a light yellow oil (4.1 g). Vacuum distillation afforded pure (>99.5% by GC) **4c** (3.24 g (0.0174 mol, 94%; bp 45 °C, 4 mm Hg (lit.⁴ 71 °C, 27 mm Hg)). This compound exhibited NMR data similar to those previously reported.⁶ ¹H NMR (CDCl₃) δ = 0.29 (s, 6H), 1.52 (s, 4H), 1.71 (s, 6H); ¹³C NMR (CDCl₃) δ = -2.5, 19.4, 26.9, 130.9; MS, *m/z* = 186 (40), 184 (31), 182 (24), 171 (60), 169 (45), 167 (36), 104 (50), 102 (38), 100 (30), 89 (100), 87 (77), 85 (58).

Steady-state Photolyses: Photolyses (254 nm) of **4a** or **4b** were carried out in septa-sealed quartz NMR tubes (5 mm) using ~0.05 M solutions of substrate in argon-saturated cyclohexane-*d*₁₂ and monitored by ¹H NMR and contained ~0.5 M methanol, acetic acid, isoprene, or triethylsilane. Conversions were typically taken to *ca.* 20% conversion (*ca.* 5 minutes total irradiation time) with periodic monitoring by NMR over the course of the photolysis. In every case the formation of the diarylgermylene adduct was accompanied by an equal yield of 2,3-dimethyl-1,3-butadiene (DMB); the identities of the diarylgermylene adducts were verified by comparison to authentic samples (see below) that were either spiked into the NMR tube or co-injected on the GC. Accurate detection of the alkoxy- (**9a-c**, **12**) and acetoxygermanes (**10a**) by GC was very difficult due to decomposition on the column. Photolysis of **4c** at 214 nm was carried out in much the same manner as for **4a** or **4b** but with lower concentrations of **4c** (~0.01

M) and trapping agent ([MeOH] = 0.035 M or [isoprene] = 0.005 M). Product conversions were typically ~5-10%. The resulting products were identified by ^1H NMR (**9c**) or co-injection with an authentic sample on the GC and GC/MS (**11c**).

Diphenyl(triethylsilyl)germane (8a) was prepared by a modification of the method of Satgé and coworkers.⁷ A flame-dried, two-necked 100 mL round-bottom flask was fitted with an addition funnel, magnetic stirrer, and a rubber septum, through which anhydrous THF (10 mL) and diphenylgermane (2.0 g, 0.0088 mol) were introduced with stirring *via* syringe. The flask was cooled to $-40\text{ }^\circ\text{C}$ (MeCN / CO_2 bath), after which a 1.7 M solution of *tert*-butyllithium in pentane (4.5 mL, 0.0077 mol) was added dropwise *via* syringe. The resulting bright yellow solution was warmed to $-20\text{ }^\circ\text{C}$ and triethylchlorosilane (1.30 mL, 0.0077 mol) was introduced. The solution was gradually warmed to room temperature over 2h, resulting in the formation of a white precipitate. The reaction was hydrolyzed with saturated aqueous ammonium chloride (15 mL), the layers were separated, and the aqueous fraction was extracted with diethyl ether (2 x 30 mL). The combined organic fractions were washed with water (1 x 25 mL), 5% aqueous sodium bicarbonate (1 x 15 mL), and again with distilled water (1 x 25 mL), dried with anhydrous magnesium sulfate, and filtered. The solvent was removed on a rotary evaporator to yield a colorless oil (3.00 g), which was distilled under vacuum to afford unreacted diphenylgermane (0.20 g; $140\text{ }^\circ\text{C}$, 0.4 mm Hg) and the desired product as a colorless oil (1.50 g, 0.0044 mol, 57%; $160\text{ }^\circ\text{C}$, 0.2 mm Hg). It was identified as **8** on the basis of the following spectroscopic data: ^1H NMR (C_6D_6), δ = 0.76 (q, 6H), 0.95 (t, 9H), 5.15 (s, 1H), 7.15-7.21 (m, 6H), 7.61-7.63 (m, 4H); ^{13}C NMR (C_6D_6), δ = 4.8, 8.4, 128.5, 128.6, 135.8, 137.9; ^{29}Si NMR (C_6D_6), δ = 2.3; IR (neat), 3067.8 (m), 3052.3 (m), 2954.8 (s), 2909.7 (s), 2876.0 (s), 1996.0 (s, Ge-H), 1482.6 (m), 1461.0 (m), 1430.9 (s), 1415.1 (w), 1235.5 (w), 1087.7 (m), 1005.8 (s), 732.2 (s), 699.0 (s), 651.9 (s);

MS (EI), m/z = 346 (3, ^{76}Ge), 344 (10, ^{74}Ge), 342 (7, ^{72}Ge), 340 (5, ^{70}Ge), 333 (25), 331 (100), 329 (75), 327 (50), 303 (16), 301 (12), 299 (9), 229 (47), 228 (95), 227 (78), 226 (75), 225 (56), 224 (52), 183 (17), 151 (57), 149 (47), 147 (27), 107 (26), 87 (26); Exact mass: calc. for $\text{C}_{18}\text{H}_{26}\text{GeSi}$, 344.1016; found, 344.1015.

Preparation of methoxydiphenylgermane (9a): This compound has been previously reported, but was not described in complete detail.^{8,9} The synthesis of **9a** was accomplished by a preparative irradiation employing 6 RPR-2537 lamps housed in a Rayonet Photochemical Reactor (Southern New England Ultraviolet Co.). A solution of **4a** (1.60 g, 0.0052 mol) in anhydrous methanol/diethyl ether (1:1 v/v, 15 mL) was added to a quartz photolysis tube, sealed with a rubber septum, deoxygenated with a stream of dry argon, and irradiated with periodic monitoring of the course of the photolysis by GC. The solution was re-deoxygenated every 4 hr during the photolysis. After 24 hr the ratio of **4a** to **9a** was approximately 1:7, and only **4a**, DMB, and **9a** could be detected in the photolysis mixture within the limits of sensitivity of the GC method. The reaction was stopped and the volatile components were removed on the rotary evaporator to yield a yellow oil. Vacuum distillation (112 °C, 0.1 mm Hg) yielded a colorless oil (0.27g, 0.00104 mol, 20%) which was identified as methoxydiphenylgermane (**9a**) on the basis of the following spectroscopic data: ^1H NMR (C_6D_6), δ = 3.62 (s, 3H), 6.22 (s, 1H), 7.43-7.45 (m, 6H), 7.59-7.63 (m, 4H); ^{13}C NMR (C_6D_6), δ = 54.6, 128.5, 130.2, 134.1; IR (neat) 3071.4 (m), 3053.5 (m), 2973.0 (s), 2926.4 (s), 2815.3 (m), 2037.9 (s, Ge-H), 1484.8 (m), 1433.6 (s), 1374.8 (m), 1337.1 (w), 1306.9 (w), 1097.9 (s), 1052.5 (s), 707.6 (s), 606.8 (s); MS (EI) m/z = 261 (2, ^{76}Ge), 259 (7, ^{74}Ge), 257 (5, ^{72}Ge), 255 (4, ^{70}Ge), 229 (17), 227 (17), 225 (10), 182 (12), 180 (8), 178 (5), 154 (44), 151 (32), 149 (20), 105 (12), 83 (26), 73 (100), 55 (17), 45 (90); Exact mass: calc. for (M - 1) $\text{C}_{13}\text{H}_{13}^{74}\text{GeO}$, 259.0178; found, 259.0150.

Preparation of Acetoxydiphenylgermane (10a): The synthesis of **10a** was accomplished by a preparative irradiation employing 6 RPR-2537 lamps housed in a Rayonet Photochemical Reactor (Southern New England Ultraviolet Co.). A 0.1 M solution of **4a** (0.093 g, 0.0003 mol) in 3.0 mL anhydrous hexane containing 0.5 M glacial acetic acid (0.09 g, 0.0015 mol) was added to a quartz photolysis tube, sealed with a rubber septum, deoxygenated with a stream of dry argon, and irradiated for 40 minutes. The reaction was stopped and the volatile components were removed on the rotary evaporator to yield a yellow oil. The conversion of **4a** to **10a** was approximately 75%, as determined by NMR. ^1H NMR (C_6D_6), $\delta = 1.75$ (s, 3H), 6.72 (s, 1H), 7.10-7.18 (m, 6H), 7.61-7.66 (m, 4H); ^1H NMR (C_6D_{12}), $\delta = 1.92$ (s, 3H), 6.52 (s, 1H), 7.30-7.32 (m, 6H), 7.60-7.62 (m, 4H); IR (neat) 3071 (m), 3053 (m), 2976 (w), 2924 (m), 2093 (m, Ge-H), 1754 (m), 1712 (s), 1485 (w), 1433 (s), 1368 (m), 1273 (s), 1095 (m), 920 (w), 733 (s), 697 (s)

Preparation of 1,1,2,2-tetraphenyl-1-methoxydigermane (12): A solution of 1,1,2,2-tetraphenyl-1-chlorodigermane¹⁰ (1.60 g, 0.00327 mol) in a mixture of pentane (20 mL) and benzene (2 mL) was prepared in a flame-dried apparatus consisting of a 50 mL, two-necked roundbottom flask, septum, and magnetic stirrer. The solution was cooled in an ice water bath (0 °C) and 0.0035 mol of a freshly prepared solution of NaOMe (0.08 g Na in 1.5 mL anhydrous MeOH) was added via syringe over 30 minutes with rapid stirring. After a further 30 minutes at 20 °C the cloudy-white suspension was allowed to settle, the supernatant decanted and the solvent removed on the rotary evaporator to yield 1.65 g of a colorless oil. This crude product was purified by cooling to -20 °C, where **12** formed a distinct oil free of impurities; the resulting colorless supernatant (1.32 g, 0.00272 mol, 83%) was identified as 1,1,2,2-tetraphenyl-1-methoxydigermane on the basis of the following spectroscopic data: ^1H NMR (C_6D_6), $\delta = 3.63$ (s, 3H), 5.70 (s, 1H), 7.06-7.12 (m, 12H), 7.56-7.60 (m, 8H); ^{13}C NMR (C_6D_6), $\delta = 54.4, 128.7,$

128.8, 129.3, 130.3, 134.6, 135.1, 135.9; IR (neat) 3069 (m), 3051 (m), 2958 (w), 2926 (m), 2814 (m), 2021 (s, Ge-H), 1484 (m), 1432 (s), 1186 (w), 1090 (s), 1046 (s), 735 (s), 699 (s), 662 (m), 592 (s); MS (EI) m/z = 490 (3), 489 (3), 488 (8), 487 (5), 486 (10), 485 (5), 484 (9), 483 (3), 482 (5), 408 (5), 406 (5), 305 (100), 303 (70), 301 (50), 259 (30), 257 (20), 255 (15), 229 (60), 227 (68), 225 (47), 151 (70), 149 (50), 147 (33); Exact mass: calc. for $C_{25}H_{24}Ge_2O$, 488.0262; found, 488.0251.

1,1-Dichloro-3-methyl-2,5-dihydro-1H-germole (23) was prepared analogously to the method employed for **7**. Germanium dichloride-dioxane (10.0 g, 0.043 mol) was added to 70 mL anhydrous THF, the solution was brought to a mild reflux and 2-methyl-1,3-butadiene (isoprene) (3.8 g, 0.056 mol) in 10 mL anhydrous THF was added dropwise over 1 hr. The THF was distilled off under N_2 and the remaining liquid was distilled under vacuum to yield a colorless oil. The compound was identified as **23** (6.65 g, 0.032 mol, 74%; 32 °C, 0.2 mm Hg (lit.⁴ 98 °C, 34 mm Hg)) on the basis of its 1H and ^{13}C NMR spectra: 1H NMR ($CDCl_3$), δ = 1.82 (s, 3H), 2.09 (s, 2H), 2.25 (s, 2H), 5.76 (s, 1H); ^{13}C NMR ($CDCl_3$), δ = 22.9, 27.7, 29.5, 122.7, 137.9.

3-Methyl-1,1-diphenyl-2,5-dihydro-1H-germole (11a) was synthesized in a similar fashion as **4a**. To a solution of **23** (1.42 g, 0.0067 mol) in anhydrous Et_2O (20 mL) was added $PhMgBr$ (5 mL of a 3.0 M solution in Et_2O , 0.015 mol) dropwise over 30 minutes. The resulting yellow solution was hydrolyzed and extracted with Et_2O to yield a yellow oil (1.4 g). Radial chromatography (hexanes) yielded **11a** (1.2 g, 0.0041 mol, 61%), whose ^{13}C NMR spectrum agreed well with that previously reported:¹¹ 1H NMR ($CDCl_3$) δ = 1.90 (s, 3H), 1.93 (s, 2H), 2.03 (s, 2H), 5.77 (s, 1H), 7.39-7.40 (m, 6H), 7.55-7.57 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = 19.1, 22.5, 22.7, 125.3, 128.2, 128.9, 134.1, 138.3, 140.1.

3-Methyl-1,1-bis-(2,4,6-trimethylphenyl)-2,5-dihydro-1H-germole (11b) was synthesized in a similar fashion as **4b**. To a solution of **23** (2.0 g, 0.0094 mol) in anhydrous Et₂O (20 mL) was added MesMgBr (0.021 mol, 35 mL of a 0.6 M solution in Et₂O) dropwise over 30 minutes. The resultant yellow solution was hydrolyzed, extracted with diethyl ether, dried with MgSO₄, filtered and the solvent removed on a rotary evaporator to yield of a yellow oil (3.1 g). Radial chromatography (hexanes) yielded **11b** (1.5 g, 0.004 mol, 43%): ¹H NMR (CDCl₃) δ = 1.89 (s, 3H), 2.15 (s, 2H), 2.25 (s, 2H), 2.31 (s, 6H), 2.37 (s, 12H), 5.80 (s, 1H), 6.86 (s, 4H); ¹³C NMR (CDCl₃) δ = 20.9, 24.0, 25.7, 29.3, 125.5, 128.8, 137.6, 138.0, 140.3, 143.1; IR (neat) 2945 (m), 2938 (m), 1623 (w), 1575 (m), 1450 (s), 1388 (w) 1011 (s), 1001 (m), 752 (s); MS (EI) *m/z* = 380 (1, ⁷⁴Ge), 378 (0.7, ⁷²Ge), 310 (40), 310 (25), 308 (16), 260 (6), 193 (26), 192 (100), 190 (67), 188 (33), 86 (8); Exact mass: calc. for C₂₃H₃₀Ge, 380.1559; found, 380.1570.

1,1,3-Trimethyl-2,5-dihydro-1H-germole (11c) was prepared in similar fashion to **4c**. To a solution of **23** (0.30 g, 0.0014 mol) in anhydrous Et₂O (15 mL) at 5 °C was added a solution of methyl magnesium bromide (1.07 mL of a 3.0 M solution in Et₂O, 0.0032 mol) via syringe, and the resulting mixture was stirred at room temperature for 2 h. The reaction was hydrolyzed and extracted with diethyl ether, dried with MgSO₄, filtered and the solvent was removed on a rotary evaporator to yield a colourless oil (0.25 g). Radial chromatography (hexanes) yielded **11c** (0.21 g, 0.0012 mol, 88%) which exhibited NMR data similar to those previously reported.¹² ¹H NMR (C₆D₆) δ = 0.24 (s, 6H), 1.37 (bs, 2H), 1.53 (bs, 2H), 1.80 (s, 3H), 5.70 (bs, 1H); ¹³C NMR (C₆D₆) δ = -2.1, 20.5, 22.7, 23.8, 125.8, 140.0.

Methoxydimethylgermane (9c) from (214 nm) photolysis of **4c** in cyclohexane-*d*₁₂ containing 0.035 M MeOH was identified by comparison of its ¹H NMR spectrum [δ 0.40 (d, 6H, J=2.4 Hz), 3.45 (s, 3H), 5.29 (sep, 1H, J = 2.4 Hz)] to the reported spectrum.¹⁶

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