Synthesis and Photochemistry of 1,2-Digermacyclohexa-3,5-dienes and Related Compounds

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Some new germanium analogues of 1,3-cyclohexadiene, 3,4,5,6-tetraphenyl-, 3,6-diphenyl-, and 3,4,5,6-tetramethyl-1,2-digermacyclohexa-3,5-diene and 3,4,5,6-tetraphenyl-1-germa-2-silacyclohexa-3,5-diene, were prepared and fully characterized by spectroscopic methods. On photolysis, the 1,2-digermacyclohexa-3,5-diene underwent extrusion of dialkylgermylene (R_2Ge:) to give the corresponding germacyclopentadiene. On irradiation the 1-germa-2-silacyclohexa-3,5-diene yielded preferentially the silacyclopentadiene via extrusion of R_2Ge:. The mechanism of these photolyses is discussed.

Introduction

Although photochemical isomerization of 1,3-cyclohexadienes to 1,3,5-hexatrienes has been investigated extensively in connection with the chemistry of vitamin D, with conservation of orbital symmetry, and also with preparation of a medium-sized ring,[1−6] only a few photochemical studies of the group 14 element (silicon and germanium) analogues of 1,3-cyclohexadienes have been reported. Recent studies of the photolysis of silicon analogues of 1,3-cyclohexadiene reveal interesting elemental as well as substitution effects on products formed. These were accounted for by assuming a triene-like intermediate that contains a silicon−silicon double bond.[7,8] Thus, on irradiation some 1-silacyclohexa-2,4-dienes and 1,2-disilacyclohexa-3,5-dienes have been reported to afford 1-silabicyclo[3.1.0]hex-3-ene and 4-vinyl-1-silacyclobuta-2-ene and 5,6-disilabicyclo[2.1.1]hex-2-ene and 2,6-disilabicyclo[3.1.0]hex-3-ene, respectively.

Recently, we have reported the first photochemical isomerization of one of the germanium analogues of a 1,3-cyclohexadiene, namely of a 1-germacyclohexa-2,4-diene, which yields the corresponding 4-vinyl-1-germacyclobut-2-ene.[9] We describe here the preparation, structural characterization, and photochemical transformation of some other types of germanium analogues of a 1,3-cyclohexadiene, namely 3,4,5,6-tetraphenyl-, 3,6-diphenyl-, and 3,4,5,6-tetramethyl-1,2-digermacyclohexa-3,5-diene (**1**−**3**) and 3,4,5,6-tetraphenyl-1-germa-2-silacyclohexa-2,4-diene (**4**). The photochemical behavior of these germanium analogues, **1**−**4**, has been investigated mainly by means of trapping experiments. The mechanism of these photochemical isomerizations is discussed and compared with that of silicon analogues.

Results and Discussion

Preparation and Characterization of Germanium Analogues of a 1,3-Cyclohexadiene and Re-

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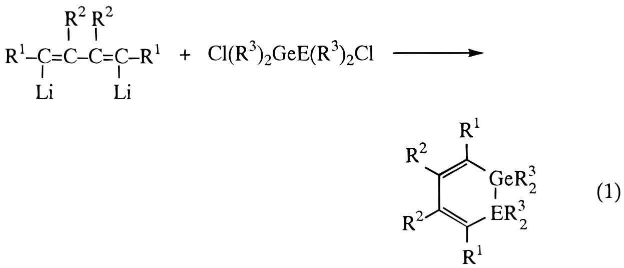
lated Compounds. Some 1,2-digermacyclohexa-3,5-dienes and 1-germa-2-silacyclohexa-3,5-diene derivatives were prepared by the reaction of an appropriate 1,4-dilithiobutadiene with 1,1,2,2-tetraalkyl-1,2-dichlorodigermane and (dialkylchlorosilyl)dialkylchlorogermane in the case of **4**, respectively.[8,10] Thus, 1,1,2,2-tetraalkyl-3,4,5,6-tetraphenyl-1,2-digermacyclohexa-3,5-dienes (**1a**, E = Ge, R^1 = R^2 = Ph, R^3 = Me; **1b**, E = Ge, R^1 = R^2 = Ph, R^3 = Et) were obtained by the reaction of 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene with the corresponding 1,1,2,2-tetraalkyl-1,2-dichlorodigermane. Similarly, 1,1,2,2-tetramethyl-3,6-diphenyl-1,2-digermacyclohexa-3,5-diene (**2**) was prepared by the reaction of 1,4-dilithio-1,4-diphenyl-1,3-butadiene with 1,1,2,2-tetramethyl-1,2-dichlorodigermane. On the other hand, 1,1,2,2,3,4,5,6-octamethyl-1,2-digermacyclohexa-3,5-diene (**3**) was prepared via 1,1-bis(η^5-cyclopentadienyl)-1,2,3,4-tetramethyl-1-zirconacyclopenta-2,4-diene.[11,12] By treatment with iodine followed by reaction of the diiodo-1,3-butadiene thus produced with *n*-butyllithium, the zirconacycle was converted to (1*Z*,3*Z*)-1,4-dilithio-1,2,3,4-tetramethly-1,3-butadiene. Reaction of the latter with 1,1,2,2-tetramethyl-1,2-dichlorodigermane afforded the 1,2-digermacyclohexa-3,5-diene **3**. 1,1,2,2-Tetraethyl-3,4,5,6-tetraphenyl-1-germa-2-silacyclohexa-3,5-diene (**4**) was prepared by the treatment of 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene with (diethylchlorosilyl)diethylchlorogermane. Germacyclohexadienes **1**, **2**, and **4** are yellow solids, and **3** is a colorless liquid.



$$R^1\text{–}\underset{\text{Li}}{C}=\overset{R^2}{C}\text{–}\overset{R^2}{C}=\underset{\text{Li}}{C}\text{–}R^1 + Cl(R^3)_2GeE(R^3)_2Cl \longrightarrow \quad (1)$$

1a (R^1=R^2=Ph, R^3=Me, E=Ge)
1b (R^1=R^2=Ph, R^3=Et, E=Ge)
2 (R^1=Ph, R^2=H, R^3=Me, E=Ge)
3 (R^1=R^2=R^3=Me, E=Ge)
4 (R^1=R^2=Ph, R^3=Et, E=Si)

The UV maxima of **1**, **2**, and **4** are located around 330 nm (**1a**, 330 nm; **1b**, 335 nm; **2**, 328 nm; **4**, 339 nm). On the other hand, the permethyl species **3**, which has no phenyl groups on the butadienyl moiety, shows its absorption maximum at much shorter wavelength, 289 nm, which is at much larger wavelength than the UV maximum of the corresponding isoelectronic, wholly organic 1,3-cyclohexadiene derivative. The characteristic red shift of absorption bands of these germacycles **1**−**4** should be ascribable to appreciable orbital interaction between the σ orbital of the Ge−Ge or Ge−Si bonds and the π orbital developed over the butadienyl moiety of 1,2-digerma- or 1-germa-2-sila-cyclohexa-3,5-diene.[8,13] In other words, the steric constraint caused by the substituents on the cyclic diene results in puckering, and this brings about the pronounced σ−π conjugation described above. However, the UV absorption of **3** is quite different from that of **1**, **2**, and **4**.

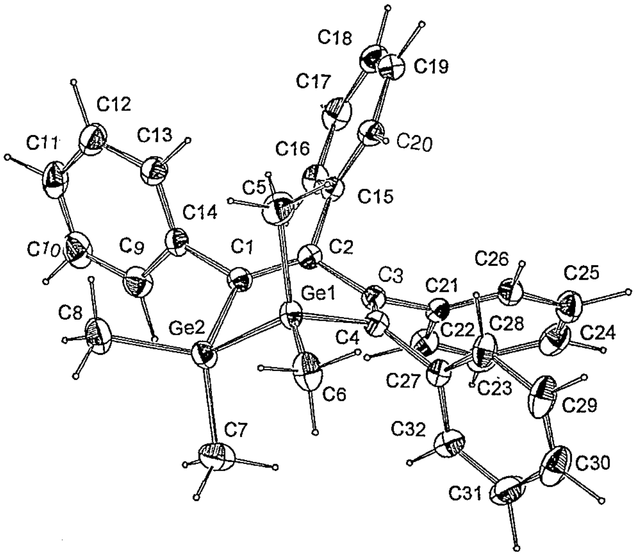


Figure 1. ORTEP drawing of the molecular structure of **1a** with atoms represented as 50% probability ellipsoids.

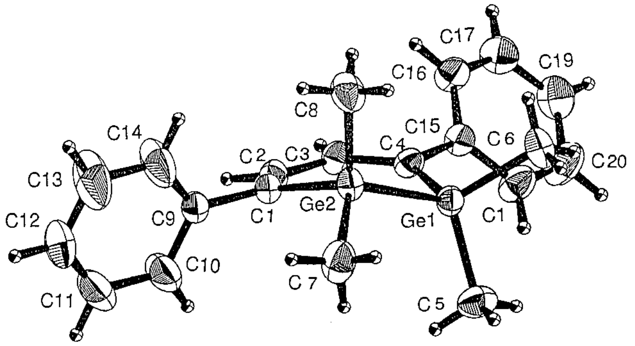


Figure 2. ORTEP drawing of the molecular structure of **2** with atoms represented as 50% probability ellipsoids.

To clarify the detailed structures of these 1,2-dimetallacyclohexadienes, X-ray analyses have been carried out on single crystals of **1a** and **2**, obtained by recrystallization from ether/acetone. ORTEP drawings of **1a** and **2** are shown in Figures 1 and 2, and the crystallographic data and structure refinement and selected bond lengths and bond angles for **1a** and **2** are listed in Tables 1 and 2, respectively. The 1,2-digermacyclohexa-3,5-diene rings of **1a** and **2** are puckered with dihedral angles of 53 and 23°, respectively, between the two planes Ge(1)−Ge(2)−C(1)−C(2) and Ge(1)−C(4)−C(3)−C(2). In addition, from the points of the σ−π conjugation mentioned above, the dihedral angles of Ge(1)−Ge(2)−C(1)−C(2) and Ge(2)−Ge(1)−C(4)−C(3) are not 0° but 50.0 and 27.1° for **1a** and 23.3 and 12.0° for **2**, respectively. This indicates that considerable orbital interaction must occur between the Ge−Ge σ bond and the π orbitals of the terminal carbon atoms C(1) and C(4). The Ge−Ge−C and Ge−C−C bond angles con-

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Table 1. Crystallographic Data for 1,2-Digermacyclo-3,5-dienes 1a and 2

chem formula	$C_{32}H_{32}Ge_2$ (**1a**)	$C_{20}H_{24}Ge_2$ (**2**)
fw	561.79	409.59
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$
a (Å)	9.839(1)	40.120(18)
b (Å)	22.960(3)	6.683(2)
c (Å)	12.821(2)	14.826(5)
β (deg)	99.606(7)	101.64(3)
V (Å^3)	2855.8(7)	3893(3)
Z	4	4
D_{calc} (g cm^{-3})	1.231	1.384
T (°C)	20	23
cryst dimens (mm)	0.6 × 0.3 × 0.7	0.3 × 0.25 × 0.25
X-radiation	Cu Kα	Mo Kα
λ (Å)	1.5418	0.710 73
data range, 2θ (deg)	$6 < 2\theta < 130$	$5 < 2\theta < 55$
scan type	$2\theta/\omega$	$2\theta/\omega$
scan width (deg)	$0.70 + \tan\theta$	$1.21 + \tan\theta$
no. of rflns recorded	4472	4478
no. of nonequiv rflns recorded	4214	4478
T_{max}, T_{min}	0.999, 0.774	0.998, 0.953
R_{merge} (on I)	0.058	0.055
no. of params refined	642	211
$R(F)$ ($F_o > 4\sigma F_o$)	0.0550	0.067
R_W (F^2) ($F_o > 4\sigma F_o$)	0.0700 for 4472 rflns	0.164 for 3212 rflns
goodness of fit	1.1224	1.076
max shift/esd in the final least-squares cycle	2.290	0.001
final max, min $\Delta\rho$ (e Å^{-3})	0.66, −0.91	0.86, −1.55

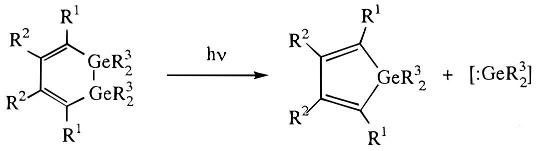
Table 2. Selected Bond Distances (Å) and Angles (deg) for 1a and 2

	1a	**2**
Ge1−Ge2	2.389(1)	2.40(2)
Ge2−C1	1.988(4)	1.95(2)
C1−C2	1.335(5)	1.35(2)
C2−C3	1.510(5)	1.48(2)
C3−C4	1.344(5)	1.35(2)
Ge1−C4	1.970(3)	1.96(2)
Ge1−C5	1.960(5)	1.97(2)
Ge1−C6	1.955(5)	1.94(2)
Ge2−C7	1.944(5)	1.95(2)
Ge2−C8	1.962(5)	1.97(2)
C1−C9	1.494(5)	1.50(2)
Ge1−Ge2−C1	93.5(1)	101.3(8)
Ge2−C1−C2	123.3(3)	123.5(8)
C1−C2−C3	124.0(3)	131.0(8)
C2−C3−C4	125.3(3)	132.3(6)
C4−Ge1−C6	110.5(2)	109.6(4)
C4−Ge1−C5	109.6(2)	111.5(5)
Ge2−Ge1−C5	111.2(2)	109.1(6)
Ge2−C1−C9	113.0(2)	117.2(8)
C2−C1−C9	123.0(3)	118.8(8)

structing the six-membered ring are in the range 93.1−93.4 and 121.6−123.4° (**1a**) and 101.0−101.3 and 122.5−123.5° (**2**), respectively. The dihedral angles and the Ge−Ge−C bond angles in **1a** are largely distorted due to steric repulsion by the four phenyl groups. The Ge−Ge bond lengths of **1a** and **2** are 2.39−2.40 Å, shorter than those of Ph_6Ge_2 (2.437 Å)[14] and cyclic polygermanes (2.45−2.48 Å).[15,16]

The most favorable geometry of $\sigma-\pi$ interaction is that in which the σ (Ge−Ge) orbital is orthogonal to the π orbital on the butadienyl groups. The X-ray structures of **1a** and **2** do not show the best geometry for $\sigma-\pi$ interaction; i.e., the dihedral angles of Ge(1)−Ge(2)−C(1)−C(2) and Ge(2)−Ge(1)−C(4)−C(3) are only 50.0 and 27.1° for **1a**. The UV absorption of **3** is quite different from those of **1a** and **2**. As expected, the phenyl groups on the butadienyl moiety strongly influence the UV maxima of the cyclic dienes as well as the $\sigma-\pi$ interaction.

Photochemistry of 1−4. We have investigated the photochemical behavior of **1**−**4** and compared it with that of silicon and carbon analogues. When a degassed C_6D_6 solution of 1,1,2,2-tetramethyl-3,4,5,6-tetraphenyl-1,2-digermacyclohexa-3,5-diene (**1a**) in a Pyrex NMR tube was irradiated with a 450-W high-pressure Hg arc lamp for 30 min at room temperature, 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (**5a**)[17] was obtained quantitatively as the sole isolable product (eq 2). One equivalent of dimethylgermylene must have been extruded from **1a** in the photolysis. In confirmation, when **1a** was photolyzed in the presence of a germylene trapping agent, 2,3-dimethylbuta-1,3-diene,[18] under similar conditions, the expected germylene trapped product, namely, 1,1,3,4-tetramethyl-1-germacyclopent-3-ene,[18] was obtained in 78% yield.



(2)

1a **5a** (quant.) (R^1=R^2=Ph, R^3=Me)
1b **5b** (98%) (R^1=R^2=Ph, R^3=Et)
3 **10** (quant.) (R^1=R^2=R^3=Me)

Similar irradiation of a C_6D_6 solution of 1,1,2,2-tetraethyl-3,4,5,6-tetraphenyl-1,2-digermacyclohexa-3,5-diene (**1b**) gave 1,1-diethyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,5-diene (**5b**) via extrusion of diethylgermylene in 98% yield. The extruded diethylgermylene was trapped in part with 2,3-dimethylbuta-1,3-diene in another experiment to give the corresponding 1-germacyclopent-3-ene in 24% yield. The remainder of the diethylgermylene was converted to miscellaneous, unidentified oligo(diethylgermylene)s.[19]

Permethylated 1,2-digermacyclohexa-3,5-diene (**3**) showed similar photochemical behavior, giving, via extrusion of Me_2Ge:, 1,1,2,3,4,5-hexamethyl-1-germacyclopenta-2,5-diene (**10**) quantitatively. On consideration of the irradiation time required to consume the starting cyclohexadienes, methyl derivative **3** may be presumed to be less reactive than tetraphenyl derivative **1**.

When diphenyl derivative **2** in degassed C_6D_6 solution in a Pyrex NMR tube was irradiated for 2 h under similar conditions, 2,5-diphenyl-1,1-dimethyl-1-germacyclopenta-2,4-diene (**6**) was produced, as expected, in 11% yield, together with the three dimers **7** (36%), **8** (14%), and **9** (8%). The photodimers **7**−**9** were isolated

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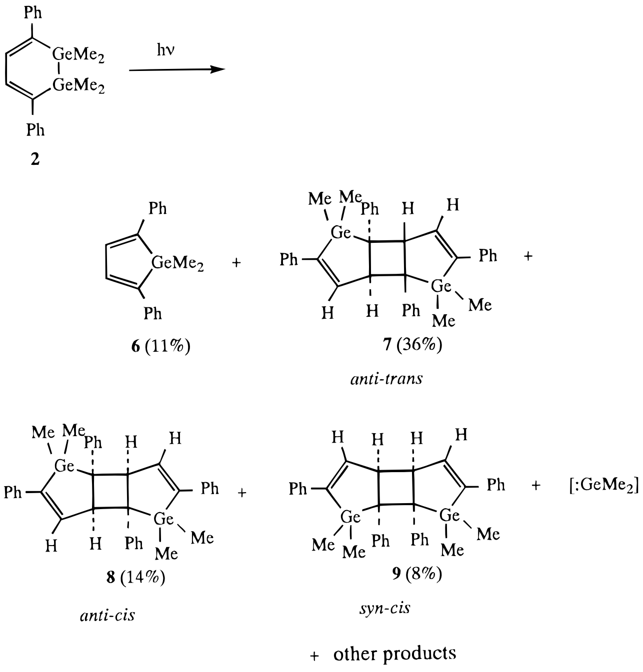

(3)

and purified by rapid chromatography with a short silica column followed by recrystallization from ethanol. The germole **6** was identified by comparing its ^{1}H NMR and MS spectra with those of an authentic sample.[17] Furthermore, photodimers **7**−**9** were characterized by their ^{1}H and ^{13}C NMR, ^{1}H−^{1}H COSY, ^{1}H−^{13}C COSY, and MS spectra. Finally, X-ray crystallographic analysis unambiguously established the structures of **7**−**9**. The photodimers **7**−**9** were assigned anti-trans, anti-cis, and syn-cis structures, respectively, by comparison of these spectral data with those of the corresponding silyl dimers.[20,21] The structures of the dimers **7**−**9** were confirmed by X-ray crystallographic analysis. Their crystal data are described in Tables 3 and 4.

ORTEP drawings of the molecular structures of **7**−**9** are presented in Figures 3−5, and selected bond lengths and bond angles are listed in Tables 3 and 4. The structural results show that two 1-germacyclopentene moieties adopt a trans configuration about the four-membered ring of **7** but a cis conformation of **8** and **9**. The four-membered rings of **7** and **8** are nearly planar, but that of **9** is slightly distorted, possibly by the steric bulk of two neighboring phenyl groups on the ring.

Under similar conditions, photolysis of **2** in the presence of 2,3-dimethylbuta-1,3-diene yielded the expected germylene trapping product 1,1,3,4-tetramethyl-1-germacyclopent-3-ene in 26% yield. 2,2,4,4,6,6-Hexamethyl-1,3,5-trioxa-2,4,6-trigermacyclohexane also was formed in 10% yield, together with trace amounts of dodecamethylcyclohexagermane (1%) and decamethylcyclopentagermane (<1%). Dimethylgermylene is readily polymerized to yield permethylated cyclic and linear oligogermanes.[22] The 1,3,5-trioxa-2,4,6-trigermacyclohexane conceivably is formed by trimerization of dimethylgermanone or its equivalent arising from oxidation of dimethylgermylene.[23]

Table 3. Crystallographic Data for [2 + 2] Photodimers 7−9

chem formula	$C_{60}H_{52}Ge_2$ (**7**)	$C_{60}H_{52}Ge_2$ (**8**)	$C_{60}H_{52}Ge_2$ (**9**)
fw	918.256	918.256	918.256
cryst syst	monoclinic	monoclinic	triclinic
space group	*C*2/*c*	*P*2/*c*	$P1_2$
a (Å)	20.995(2)	18.020(3)	12.253(2)
b (Å)	9.9414(4)	10.060(2)	13.429(1)
c (Å)	14.851(1)	17.090(2)	9.663(2)
α (deg)	90	90	95.10(2)
β (deg)	105.691(2)	90.02(1)	104.383(9)
γ (deg)	90	90	97.64(8)
V (Å^3)	2984.2(3)	3059.9(7)	1513.5(4)
Z	4	4	2
D_{calc} (g cm^{-3})	1.353	1.319	1.334
μ (Mo Kα)(mm^{-1})	2.04	1.99	1.99
T (°C)	23	23	23
cryst dimens (mm)	0.4 × 0.4 × 0.2	0.5 × 0.5 × 0.4	0.3 × 0.25 × 0.1
X-radiation	Mo Kα	Mo Kα	Mo Kα
λ (Å)	0.710 73	0.710 73	0.710 73
data range, 2θ (deg)	$5 < 2\theta < 55$	$5 < 2\theta < 55$	$5 < 2\theta < 55$
scan type	2θ/ω	2θ/ω	2θ/ω
scan width (deg)	1.5 + 0.35 tan θ	1.5 + 0.35 tan θ	1.5 + 0.35 tan θ
no. of rflns recorded	9204	7033	6917
no. of nonequiv rflns recorded	3145	7029	6916
T_{max}, T_{min}	1.000, 0.540	1.000, 0.382	1.000, 0.609
R_{merge} (on *I*)	0.058	0.058	0.055
no. of params refined	182	355	343
R(*F*) ($F_o > 4\sigma F_o$)	0.042	0.075	0.055
$R_W(F^2)$ ($F_o > 4\sigma F_o$)	0.102 for 2222 rflns	0.194 for 4513 rflns	0.136 for 4574 rflns
goodness of fit	1.070	1.004	1.001
max shift/esd in the final least-squares cycle	0.000	0.000	0.000
final max, min Δρ (e Å^{-3})	0.57, −0.58	1.31, −1.33	0.90, −0.83

To show clearly that the photodimers **7**−**9** were derived from the photodimerization of **6** formed during the photolysis of **2**, **6** was independently irradiated with a 450 W high-pressure Hg arc lamp in C_6D_6 for 2 h. The three [2 + 2] photodimers **7**−**9** were produced in a 4:2:1 ratio (eq 4). Only the *anti-trans* photodimer **7** had been

$$\mathbf{6} \underset{<300\text{ nm}}{\overset{>300\text{ nm}}{\rightleftharpoons}} \mathbf{7},\ \mathbf{8},\ \text{and}\ \mathbf{9} \qquad (4)$$

reported as the product of the photoirradiated **6** in ether.[20] While the organosilicon photoproducts of types **7**−**9** were fairly stable thermally under photoirradiation with a medium-pressure Hg arc lamp,[21] irradiation of degassed C_6D_6 solutions of the germanium compounds **7**−**9** in a quartz NMR tube with a low-pressure Hg arc lamp afforded 1-germacyclopenta-2,4-diene **6**, giving the reaction mixture composed of **6** and the three dimers. Thus, the [2 + 2] photodimers **7**−**9** undergo photochemical cycloreversion to give germacyclopentadiene **6** on irradiation with a low-pressure Hg arc lamp.

Thus, 2,5-diphenyl-1-germacyclopenta-2,4-diene **6** is readily dimerized upon irradiation, but in contrast the tetraphenyl derivative **5a** is photochemically stable under similar irradiation conditions. This probably is attributable to the steric hindrance caused by phenyl

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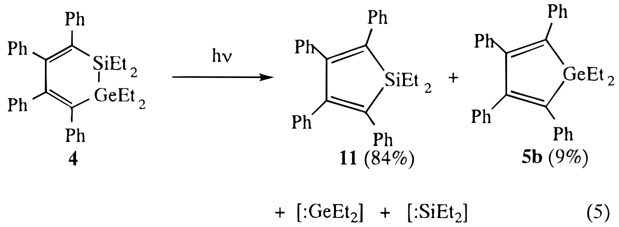
Table 4. Selected Bond Distances (Å) and Angles (deg) for Dimers 7−9[a]

			Dimer **7**				
Ge1−C18	1.945(4)	C1−C2#	1.586(4)	C1−C11	1.499(5)	C3−C4	1.334(5)
Ge1−C4	1.952(3)	C2−C3	1.500(5)	C1−C2	1.562(4)	C4−C5	1.469(5)
Ge1−C1	1.992(3)	C2−C1#	1.586(4)				
C18−Ge1−C4	116.0(2)	C18−Ge1−C17	108.6(2)	C2−C1−Ge1	103.7(2)	C2#−C1−Ge1	113.2(2)
C4−Ge1−C17	112.2(2)	C18−Ge1−C1	114.2(2)	C3−C2−C1	113.0(3)	C3−C2−C1#	121.8(3)
C4−Ge1−C1	91.42(14)	C17−Ge1−C1	113.8(2)	C1−C2−C1#	90.0(2)	C4−C3−C2	121.5(3)
C11−C1−C2	117.4(3)	C11−C1−C2#	119.9(3)	C3−C4−C5	125.1(3)	C3−C4−Ge1	108.7(3)
C2−C1−C2#	90.0(2)	C11−C1−Ge1	110.3(2)	C5−C4−Ge1	126.2(3)		
			Dimer **8**				
Ge1−C18	1.916(8)	Ge2−C18B	1.954(8)	Ge2−C17B	1.945(7)	C1−C2	1.567(8)
Ge1−C4	1.932(6)	Ge2−C4B	1.963(6)	C1−C2B	1.583(8)	C2−C3	1.501(9)
Ge1−C17	1.959(8)	Ge1−C1B	2.005(6)	C2−C1B	1.555(8)	C3−C4	1.333(8)
Ge1−C1	1.978(5)	C1−C11	1.514(8)	C4−C5	1.500(8)		
C18−Ge1−C4	115.4(4)	C18−Ge1−C17	106.0(4)	C2−C1−C2B	88.9(4)	C11−C1−Ge1	109.1(4)
C4−Ge1−C17	112.5(3)	C18−Ge1−C1	119.7(3)	C2−C1−Ge1	105.1(4)	C2B−C1−Ge1	121.4(4)
C4−Ge1−C1	91.1(2)	C17−Ge1−C1	111.9(3)	C3−C2−C1B	118.7(5)	C3−C2−C1	112.6(5)
C17B−Ge2−C18B	107.3(4)	C17B−Ge2−C4B	110.5(3)	C1B−C2−C1	91.8(4)	C4−C3−C2	120.2(6)
C18B−Ge2−C4B	115.8(4)	C17B−Ge2−C1B	120.8(3)	C3−C4−C5	123.7(6)	C3−C4−Ge1	110.9(4)
C18B−Ge2−C1B	110.8(3)	C4B−Ge2−C1B	91.5(2)	C5−C4−Ge1	125.2(4)		
C11−C1−C2	117.3(5)	C11−C1−C2B	113.7(5)				
			Dimer **9**				
Ge1−C18	1.960(5)	Ge2−C18B	1.951(5)	Ge2−C17B	1.951(4)	C1−C2	1.571(6)
Ge1−C4	1.932(6)	Ge2−C4B	1.970(5)	C2−C3	1.502(6)	Ge2−C1B	2.038(4)
Ge1−C17	1.946(5)	C2−C2B	1.574(6)	C3−C4	1.342(6)	C1−C1B	1.619(6)
Ge1−C1	1.980(4)	C1−C11	1.496(6)	C4−C5	1.480(6)		
C18−Ge1−C4	109.3(2)	C18−Ge1−C17	108.0(3)	C2−C1−C1B	91.8(2)	C11−C1−Ge1	113.2(3)
C4−Ge1−C17	119.5(2)	C18−Ge1−C1	110.2(2)	C2−C1−Ge1	103.4(3)	C1B−C1−Ge1	121.8(3)
C4−Ge1−C1	90.8(2)	C17−Ge1−C1	118.0(2)	C3−C2−C1	111.0(4)	C3−C2−C2B	115.7(4)
C17B−Ge2−C18B	104.8(2)	C17B−Ge2−C4B	112.9(2)	C4−C3−C2	121.3(4)	C2B−C2−C1	90.1(3)
C18B−Ge2−C4B	112.4(2)	C17B−Ge2−C1B	124.7(2)	C3−C4−C5	123.9(4)	C3−C4−Ge1	108.5(3)
C18B−Ge2−C1B	110.1(2)	C4B−Ge2−C1B	91.8(2)	C5−C4−Ge1	127.6(3)		
C11−C1−C2	116.0(4)	C11−C1−C1B	112.4(3)				

[a] Symmetry transformations used to generate equivalent atoms: (#) $-x + {}^1/_2, -y + {}^1/_2, -z$.

groups on the C_3 and C_4 positions of the five-membered ring. Furthermore, on prolonged irradiation of a C_6D_6 solution of 1,1,2,3,4,5-hexamethyl-1-germacyclopenta-2,4-diene (**10**) with a high-pressure Hg arc lamp, none of the [2 + 2] photodimers of **10** could be detected by NMR and GC−MS spectroscopy. This also may be due to the steric hindrance of the methyl groups on C_3 and C_4 of the ring.

To examine the effect of the metalloidal element on the photochemical behavior of 1,2-dimetallacyclohexadiene, 1,1,2,2-tetraethyl-3,4,5,6-tetraphenyl-1-germa-2-silacyclohexa-3,5-diene (**4**) in benzene was irradiated with a high-pressure Hg arc lamp. The main photolysis product was 1,1-diethyl-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene (**11**) accompanied by a small amount of 1,1-diethyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (**5b**). In comformity with the results above, diethylgermylene was readily trapped with 2,3-dimethylbuta-1,3-diene as the corresponding 1-germacyclopent-3-ene in 37% yield. However, the trapping product originating from diethylsilylene could not be detected; probably the silylene is generated in too smaller quantity to be detected. In the photolysis of **4**, the preferential formation of silole **11** and diethylgermylene may be rationalized in terms of the difference in the bond dissociation energy of a Ge−C vs that of a Si−C bond[24,25] and of the stability of germyl and silyl radicals.[26]



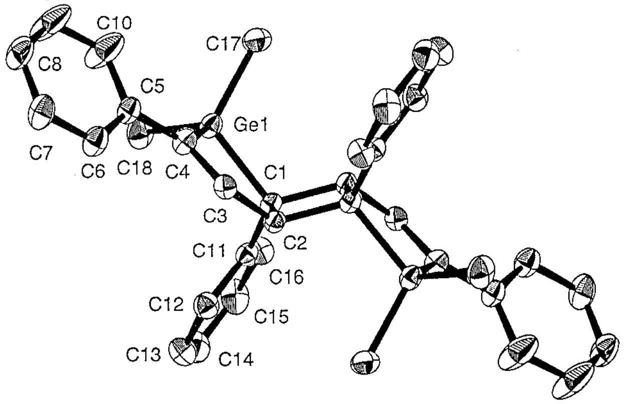


Figure 3. ORTEP drawing of the molecular structure of **7** with atoms represented as 50% probability ellipsoids. All hydrogens have been omitted for clarity.

Mechanistic Considerations. In contrast to the 1,2-disilacyclohexadiene, 1,2-digerma- and 1-germa-2-

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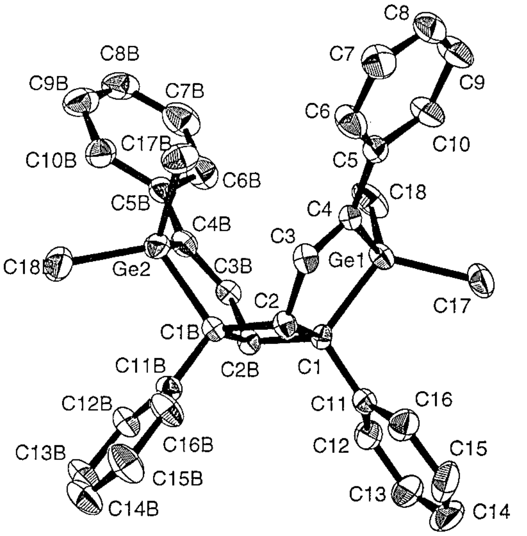
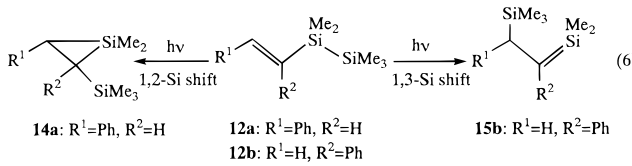
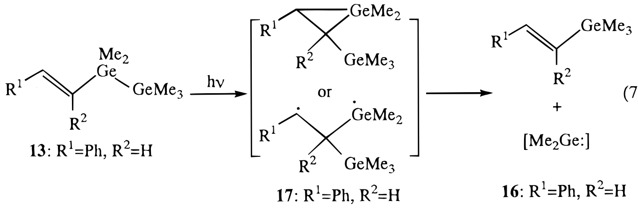


Figure 4. ORTEP drawing of the molecular structure of **8** with atoms represented as 50% probability ellipsoids. All hydrogens have been omitted for clarity.



(6)



(7)

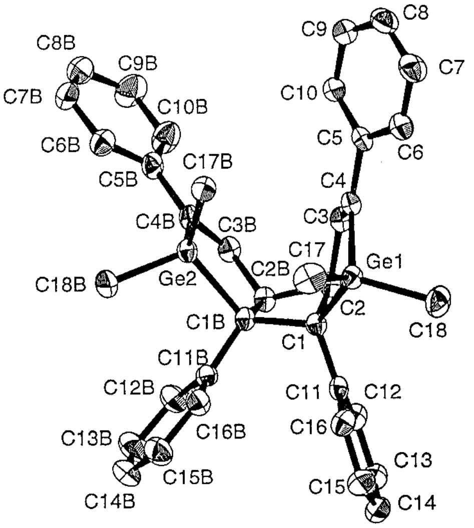


Figure 5. ORTEP drawing of the molecular structure of **9** with atoms represented as 50% probability ellipsoids. All hydrogens have been omitted for clarity.

silacyclohexadienes **1**−**4** undergo a photoinduced ring contraction reaction with extrusion of the corresponding germylene. This reminds us of the photochemistry of vinyldisilane and -digermane. The vinyldisilane **12** is transformed to either the corresponding silacyclopropane **14** or silene **15** via 1,2- or 1,3-Si migration, respectively (eq 6),[27−34] but in contrast, the vinyldigermane **13** is converted to vinylgermane **16** with extrusion of the corresponding germylene via 1,2-Ge migration or possibly a germacyclopropane or its equivalent **17** (eq 7).[35] On the other hand, one of the silicon analogues of 1,3-cyclohexadiene, namely a 1,2-disilacyclohexa-3,5-diene, has been reported to undergo quantitative photochemical isomerization to afford 2,6-disilabicyclo[3.1.0]-hex-3-ene and 5,6-disilabicyclo[2.1.1]hex-2-ene, possibly by way of a conjugated disilatriene intermediate.[10] Since disilacycles are rather photochemically stable and only undergo efficient photochemical interconversion via photoinduced 1,3-Si migration, on photolysis of the 1,2-disilacyclohexadiene the silacyclopentadiene is formed in just a trace amount after prolonged irradiation. From consideration of the photochemistry of vinyldisilane **12** and -digermane **13**, the novel photochemical behavior of **1**−**4** could be accouned for in terms of the characteristic properties of the germanium atom, as depicted in Scheme 1.

Germanium-containing dimetallacyclohexadienes **1**−**4** are expected to be readily converted to bicyclic compounds **19**, **19′**, and **20** (E = Ge, Si) via facile cyclization of dimetallotriene intermediate **18** (E = Ge, Si). In comparison with a silacyclopropane, a germacyclopropane is much more strained and labile due to its longer and weaker C−Ge bonds.[25,36] Thus, bicycles **19** and/or **19′** with a germacyclopropane ring would expel the corresponding germylene much more readily to yield a metallacyclopentadiene, as was observed. Since a germyl radical will be thermodynamically more stable than silyl and carbon radicals,[26] another possibility would be extrusion of a germylene from a germacyclopropane equivalent such as the biradical **19″** (E = Ge, Si), which contains a more stable (5)-membered silacycle that could be formed directly from dimetallotriene intermediate **18** (E = Ge, Si).

Hence, on the photolysis of **4**, one would expect that the silacyclopentadiene should be formed preferentially, possibly by way of **19″** (E = Si), which contains a more stable germyl radical and five-membered silacycle. However, the dimetallatriene **18** and bicyclic intermediates **19** and **20** could not be detected by either NMR spectroscopy or trapping experiments using methanol and chloroform under these conditions.

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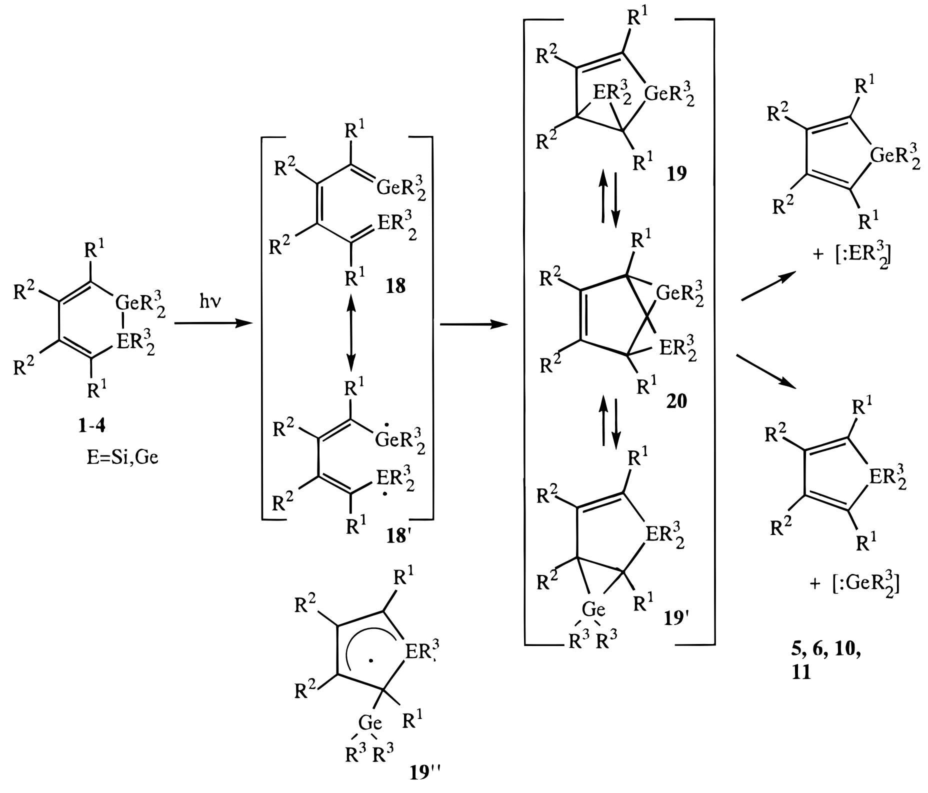
Scheme 1



Experimental Section

General Methods. All photochemical reactions were carried out in a degassed NMR tube. THF and C_6D_6 were dried by refluxing over sodium benzophenone ketyl and distilled immediately before use. Chloroform, methanol, and 2,3-dimethylbuta-1,3-diene were distilled before use. NMR spectra were obtained on a Varian Unity Inova 400 MHz NMR spectrometer. GC−MS spectra were measured on a JEOL JMS-DX 303 mass spectrometer. The infrared spectra were recorded with a Shimadzu FT IR 4200 spectrometer. The UV and UV−vis spectra were recorded on a Shimadzu UV 2200 spectrometer. Gas chromatography was performed on a Shimadzu GC 8A with a 1 m 20% SE30 column. Liquid chromatography was performed on a Twincle with an Asahipak GS 310 column. X-ray crystallographic data and diffraction intensities were measured on a four-cycle Enraf-Nonius CAD-4 diffractometer using Cu Kα ($\lambda = 1.6518$ Å) radiation or a Rigaku AFC6/S diffractometer utilizing Mo Kα ($\lambda = 0.71073$ Å) radiation with a graphite monochromator. The structures were solved by direct methods using the program system MULTAN 78. Calculations were carried out on a FACOM M-780 with UNICS III.

Materials. Diphenylacetylene, *n*-butyllithium, and lithium metal were commercially available. Dimethyldichlorogermane,[37] diethyldichlorogermane,[38] diethyldichlorosilane,[39] 1,1,2,2-tetramethyl-1,2-dichlorodigermane,[40] 1,1,2,2-tetraethyl-1,2-dichlorodigermane,[41] 1,4-dibromo-1,4-diphenylbuta-1,3-diene,[42] (1*Z*,3*Z*)-1,4-diiodo-1,2,3,4-tetramethylbuta-1,3-diene,[11,12] 1,1-dimethyl-2,5-diphenyl-1-germacyclopenta-2,4-diene,[43] 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germapenta-2,4-diene,[44] 1,1-diethyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene,[45] 1,1-diethyl-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene,[46] 1,1,2,3,4,5-hexamethyl-1-germacyclopenta-2,4-diene,[47] 1,1,3,4-tetramethyl-1-germacyclopent-3-ene,[48] 1,1-diethyl-3,4-dimethyl-1-germacyclopent-3-ene,[49] and 1,1,2,2-tetramethyl-3,4-diphenyl-1,2-digermacyclohexa-3,5-diene[10] were prepared as reported in the literature.

Preparation of (Diethylchlorogermyl)diethylchlorosilane. Into a mixture of (phenyldiethylsilyl)phenyldiethylgermane (16.7 g, 45 mmol) and a catalytic amount of $AlCl_3$ (0.1 g) in anhydrous benzene (200 mL) was bubbled HCl gas, generated from concentrated HCl and NH_4Cl, at 40 °C for 3 h. The chlorodephenylation reaction was monitored by means of GC. After the solvent was evaporated, the residue was distilled under reduced pressure to give (diethylchlorosilyl)-diethylchlorogermane (12.1 g, 42 mmol, 93%): bp 150 °C/2 mmHg; ^{1}H NMR (C_6D_6) δ 0.82−1.08 (m, 10H), 1.08−1.24 (m, 10H); ^{13}C NMR (C_6D_6) δ 7.6, 9.4, 9.6, 10.2, 10.4, 13.0, 13.3. Anal. Calcd for $C_8H_{20}Cl_2SiGe$: C, 33.38; H, 7.00. Found: C, 33.52: H, 7.20.

Preparation of 1,1,2,2-Tetramethyl-3,4,5,6-tetraphenyl-1,2-digermacyclohexa-3,5-diene (1a). A mixture of lithium metal (0.5 g, 0.072 mol) and diphenylacetylene (13 g, 0.072 mol) in anhydrous diethyl ether was stirred for 16 h at room temperature. To this solution was added anhydrous ether (150 mL) and then dimethyldichlorogermane (10.0 g, 0.036 mol) in ether (20 mL). After it was refluxed for 3 h, the mixture was hydrolyzed with water. The organic layer was extracted with diethyl ether and dried over Na_2SO_4. After the

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solvent had been evaporated, the residue was diluted with acetone to cause crystallization of pure 1,1,2,2-tetramethyl-3,4,5,6-tetraphenyl-1,2-digermacyclohexa-3,5-diene (5.14 g, 09.1 mmol, 25%): mp 175−176 °C; ^{1}H NMR (C_6D_6) δ 0.54 (s, 12H), 6.7−7.3 (m, 20H); ^{13}C NMR (C_6D_6) δ −3.7, 124.4, 125.5, 127.6, 129.8, 130.0, 140.7, 143.4, 145.1, 149.4; MS *m*/*z* 564 (^{74}Ge); UV (cyclohexane) $\lambda_{\max}$ 330.4 nm (log ϵ 3.46). Anal. Calcd for $C_{32}H_{32}Ge_2$: C, 68.41; H, 5.74. Found: C, 68.58: H, 5.62.

Preparation of 1,1,2,2-Tetraethyl-3,4,5,6-tetraphenyl-1,2-digermacyclohexa-3,5-diene (1b). A mixture of lithium metal (0.5 g, 0.072 mol) and diphenylacetylene (13 g, 0.072 mol) in anhydrous diethyl ether was stirred for 16 h at room temperature. To this solution was added anhydrous diethyl ether (150 mL) and then diethyldichlorogermane (12.0 g, 0.036 mol) in ether (20 mL). After it was refluxed for 3 h, the mixture was hydrolyzed with water. The organic layer was extracted with ether and dried over Na_2SO_4. After the solvent had been evaporated, the residue was diluted with acetone and this solution was allowed to stand at room temperature. Pure 1,1,2,2-tetraethyl-3,4,5,6-tetraphenyl-1,2-digermacyclohexa-3,5-diene (5.14 g, 0.0091 mol, 25%) was obtained: mp 175−176 °C; ^{1}H NMR (C_6D_6) δ 1.06−1.12 (m, 4H), 1.21−1.31 (m, 16H), 6.64−7.10 (m, 20H); ^{13}C NMR (C_6D_6) δ 7.19, 11.28, 124.97, 125.77, 127.31, 128.10, 128.67, 130.27, 141.53, 142.45, 143.67, 153.49; MS *m*/*z* 618 (^{74}Ge); UV (cyclohexane) $\lambda_{\max}$ 338.0 nm (log ϵ 3.72). Anal. Calcd for $C_{34}H_{36}Ge_2$: C, 69.23; H, 6.15. Found: C, 69.45: H, 6.24.

Preparation of 1,1,2,2,3,4,5,6-Octamethyl-1,2-digermacyclohexa-3,5-diene (3). To a solution of (1*Z*,3*Z*)-1,4-diiodo-1,2,3,4-tetramethylbuta-1,3-diene (3.39 g, 9.36 mmol) in 75 mL of ether at −78 °C was added with stirring 11.5 mL of 1.62 N *n*-butyllithium. This solution was stirred at −78 °C for 2 h, after which time the solution was warmed to 25 °C for 15 min. To the dilithio compound was added 1,1,2,2-tetramethyldichlorodigermane (2.6 g, 8.5 mmol) in 75 mL of ether. After it was stirred at room temperature for 90 min, the mixture was hydrolyzed with water. The organic layer was extracted with ether and dried over $MgSO_4$. After the solvent had been evaporated, the residue was distilled under reduced pressure to give 1,1,2,2,3,4,5,6-octamethyl-1,2-digermacyclohexa-3,5-diene (1.0 g, 3.2 mmol, 37.6%): bp 63 °C/1 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 12H), 1.75 (s, 3H), 1.76 (s, 3H), 1.82_7 (s, 3H), 1.82_9 (s, 3H); ^{13}C NMR ($CDCl_3$) δ −5.0, 18.4, 18.6, 123.0, 145.0; MS *m*/*z* 314 (^{74}Ge); UV (cyclohexane) $\lambda_{\max}$ 284.8 nm (log ϵ 2.52). Anal. Calcd for $C_{12}H_{24}Ge_2$: C, 45.97; H, 7.72. Found: C, 46.12: H, 7.82.

Preparation of 1,1,2,2-Tetraethyl-3,4,5,6-tetraphenyl-1-germa-2-silacyclohexa-3,5-diene (4). Compound **4** was prepared according to a method similar to that used for the preparation of **1**. To a solution of 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene was added (diethylchlorosilyl)diethylchlorogermane (11.1 g, 39 mmol) in ether (10 mL). After it was refluxed for 2 h, the mixture was hydrolyzed with water. The organic layer was extracted with diethyl ether and dried over Na_2SO_4. After the solvent had been evaporated, the residue was diluted with acetone and this solution was allowed to stand at room temperature. Pure 1,1,2,2-tetraethyl-3,4,5,6-tetraphenyl-1-germa-2-silacyclohexa-3,5-diene (10.5 g, 18.4 mmol, 47%) was obtained: mp 152 °C; ^{1}H NMR (C_6D_6) δ 0.83−0.93 (m, 2H), 1.02−1.18 (m, 10H), 1.18−1.29 (m, 8H), 6.60−7.30 (m, 20H); ^{13}C NMR (C_6D_6) δ 4.8, 6.1, 9.0, 10.7, 124.4, 124.6, 125.2, 125.3, 126.7, 126.8, 127.3, 127.5, 128.0, 128.5, 129.8, 140.1, 141.8, 142.0, 142.9, 143.8, 145.1, 150.1, 153.5; MS *m*/*z* 573 (^{74}Ge); UV (cyclohexane) $\lambda_{\max}$ 338.6 nm (log ϵ 3.59). Anal. Calcd for $C_{34}H_{36}SiGe$: C, 74.88; H, 6.65. Found: C, 74.92: H, 6.72.

Photolysis of 1, 3, and 4. As a representative example, the photochemical reaction of **1a** is described. 1,2-Digermacyclohexa-3,5-diene **1** (30 mg) was dissolved in C_6D_6 (500 μL) in a Pyrex NMR tube. The NMR tube was degassed under vacuum and sealed. The sample was irradiated with a 450 W high-pressure Hg arc lamp for 30 min at room temperature. NMR, GC, and GC−MS analysis of the resulting mixture showed 1-germacyclopenta-2,4-diene **5a** (100%) was produced.

Photolysis of 2. A degassed sealed quartz tube containing a benzene (10 mL) solution of diphenyl derivative **2** (0.3 mg) was irradiated with a 450 W high-pressure Hg arc lamp for 3 h. NMR, GC, and GC−MS analysis of the resulting mixture showed the presence of 1-germacyclopenta-2,4-diene **6** (11%), the three dimeric products **7** (36%), **8** (14%), and **9** (8%), and 2,2,4,4,6,6-hexamethyl-1,3,5-trioxa-2,4,6-trigermacyclohexane (10%), dodecamethylcyclohexagermane (1%), and decamethylcyclopentagermane (<1%). **7**: NMR (C_6D_6) δ −0.02 (s, 3H), 0.46 (s, 3H), 4.45 (d, *J* > 0.1 Hz, 1H), 6.98−7.31 (m, 11H); ^{13}C NMR (C_6D_6) δ −3.47, −1.99, 47.21, 54.17, 124.15, 126.86, 126.98, 128.78, 140.72, 142.75, 144.70, 147.20; IR (KBr, cm^{-1}) 1236; MS *m*/*z* 616 (^{74}Ge). **8**: NMR (C_6D_6) δ −0.12 (s, 3H), 0.58 (s, 3H), 4.26 (d, *J* > 0.1 Hz, 1H), 6.90−7.21 (m, 11H); ^{13}C NMR (C_6D_6) δ −3.50, −2.01, 43.21, 50.17, 122.10, 125.86, 126.98, 128.78, 140.72, 142.75, 144.70, 147.00; IR (KBr, cm^{-1}) 1235; MS *m*/*z* 616 (^{74}Ge); **9**: NMR (C_6D_6) δ 0.04 (s, 3H), 0.08 (s, 3H), 4.36 (d, *J* > 0.1 Hz, 1H), 6.87−7.20 (m, 11H); ^{13}C NMR (C_6D_6) δ −1.47, 0.99, 49.20, 56.16, 125.10, 127.82, 127.96, 129.72, 141.62, 143.55, 145.60, 148.10; IR (KBr, cm^{-1}) 1241; MS *m*/*z* 616 (^{74}Ge). The ^{1}H−^{1}H COSY spectra of **7**−**9** show that the allylic protons δ 4.26−4.45 ppm couple with the aromatic protons at δ 6.98−7.31 ppm. The ^{1}H−^{13}C COSY spectra of **7**−**9** were also observed, but C−H shifts of the aromtic rings have not yet been confirmed.

Photolysis of 1−4 in the Presence of 2,3-Dimethylbuta-1,3-diene. A degassed sealed Pyrex NMR tube containing **1a** (30 mg), 2,3-dimethylbuta-1,3-diene (100 μL), and C_6D_6 (500 μL) was irradiated with a 450 W high-pressure Hg arc lamp for 30 min at room temperature. NMR, GC, and GC−MS analysis of the resulting mixture showed that **5a** (96%) and 1,1,2,3-tetramethyl-1-germacyclopent-3-ene (78%) were formed.

Photolysis of 1−4 in the Presence of Chloroform. A degassed sealed Pyrex NMR tube containing **1a** (30 mg), chloroform (200 μL), and C_6D_6 (500 μL) was irradiated with a 450 W high-pressure Hg arc lamp for 30 min at room temperature. NMR, GC, and GC−MS analysis of the resulting mixture showed that **5a** (96%) was formed.

Photolysis of 1,1-Dimethyl-2,5-diphenyl-1-germacyclopenta-3,5-diene. A degassed sealed quartz tube containing a benzene (10 mL) solution of 1-germacyclopenta-3,5-diene (0.3 mg) was irradiated with a 450 W high-pressure Hg arc lamp for 3 h. The reaction mixtures were poured into methanol. An undissolved white powder remained and was identified by NMR in C_6D_6 and MS spectra to be the anti-trans [2 + 2] dimer (36%). The methanol solution was chromatographed on octadecyl-functionalized silica gel to give the anti-cis (14%) and syn-cis [2 + 2] dimers (8%).

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Supporting Information Available: Tables giving crystallographic data, positional and thermal parameters, and bond distances and angles and figures giving additional views and packing diagrams for **1a**, **2**, and **7**−**9**, additional 2D NMR spectra for **7**, and plots and figures analyzing dihedral angles (56 pages). Ordering information is given on any current masthead page.

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