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Photoinduced Electron Transfer from Tetraphenyl-Substituted 1,2-Digermacyclohexa-3,5-dienes and Related Compounds to C_{60}

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The irradiation of benzene–benzonitrile solutions of 3,4,5,6-tetraphenyl-substituted 1,2-digermacyclohexa-3,5-dienes and related compounds in the presence of C_{60} afforded the corresponding ring-contracted products, namely 1-germacyclopenta-2,4-dienes, with the extrusion of germylene and ring-expanded oxadigerma compounds, namely 1-oxa-2,7-digermacyclohepta-3,5-dienes. The laser flash photolysis of a benzene–benzonitrile solution of 1,2-digermacyclohexa-3,5-dienes in the presence of C_{60} showed that the transient absorption band of the C_{60} triplet state (${}^{T}C_{60}^{*}$) appeared immediately at 730 nm. With the decay of ${}^{T}C_{60}^{*}$, the absorption bands of the radical anion of $C_{60}{\cdot}^{-}$ appeared at 1060 nm, showing that an electron transfer takes place from 1,2-digermacyclohexa-3,5-dienes to ${}^{T}C_{60}^{*}$. The formation of cyclic oxadigerma compounds was explained by processes of both the photooxidation of 1,2-digermacyclohexa-3,5-dienes in the absence of C_{60} with singlet oxygen and oxidation of the cation radical of 1,2-digermacyclohexa-3,5-dienes with triplet oxygen.

Organometallic compounds, particularly those with metal–metal σ bonds, are excellent electron donors. As electron-rich species, they are subject to cleavage by various organic electrophiles as well as transition-metal complexes.[1—3] Since group-14 element (silicon and germanium) catenates have rather low ionization potentials,[4—11] the electron-transfer mechanisms are very important, in which the rate is limited by the ability of the group-14 element catenates to transfer an electron to an electrophile acting as an electron acceptor.

On the other hand, a study of how the photoexcited fullerenes act as good electron acceptors has been reported.[12—22] In the cases of C_{60} and C_{70}, the initial steps of the photoinduced electron-transfer reactions have been investigated by photochemical techniques, such as laser flash photolysis, by measuring the quenching rates of the triplet states of C_{60} and C_{70} in the visible regions. By these methods, it was found that a electron transfer took place via the triplet state of C_{60} (${}^{T}C_{60}^{*}$) and C_{70} (${}^{T}C_{70}^{*}$) in a polar solvent.

In this paper, we consider whether 1,2-digermacyclohexa-3,5-diene derivatives with low ionization potentials (IP's) act as photoinduced electron donors with respect to C_{60} or not. We also consider on the mechanism of a photoinduced electron transfer from 1,2-digermacyclohexa-3,5-diene derivatives to C_{60} with a product analysis and laser flash photolysis technique which gives direct evidence for an electron transfer.

Results and Discussion

Photoinduced Electron Transfer from 1,2-Digermacyclohexa-3,5-dienes and Related Compounds to C_{60}. The 3,4,5,6-tetraphenyl-substituted 1,2-digermacyclohexa-3,5-dienes (**1** and **2**), 1,2-disilacyclohexa-3,5-diene (**3**), and 1-sila-2-germacyclohexa-3,5-diene (**4**) used in this study were prepared from the reactions of 1,4-dilithio-1,2,3,4-tetraphenylbuta-1,3-diene, derived from diphenylacetylene and lithium metal, with 1,2-dichloro-1,1,2,2-tetraalkyldigermanes, 1,2-dichloro-1,1,2,2-tetraethyldisilane, and chlorodiethyl(chlorodiethylgermyl)silane, respectively.[23—25] All of compounds **1**—**4** are a yellow solid, are stable in air at room temperature, and can be purified by recystallization. The threshold energies (E_{th}) of the group-14 element-group-14 element bonds measured by UPS and the absorption maxima ($\lambda_{\max}$) of **1**—**4**, prepared by the above-mentioned methods, are summarized in Table 1. Compounds **1**—**4** have a low E_{th} (5.0—5.3 eV) and characteristic absorption bands of around 330 nm.

The irradiation of a degassed mixed solvent of benzene and benzonitrile (4 : 1) of 1,1,2,2-tetramethyl-3,4,5,6-tetraphenyl-1,2-digermacyclohexa-3,5-diene (**1**) in the presence of C_{60} with a sodium lamp (> 420 nm) for 10 h at room temperature resulted in the formation of the corresponding 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (**5**) (69%) and 2,2,7,7-tetramethyl-3,4,5,6-tetraphenyl-1-oxa-

Table 1. Threshold Energies (E_{th}) and UV Data for 1,2-Digermacyclohexa-3,5-dienes and Related Compounds **1**—**4**

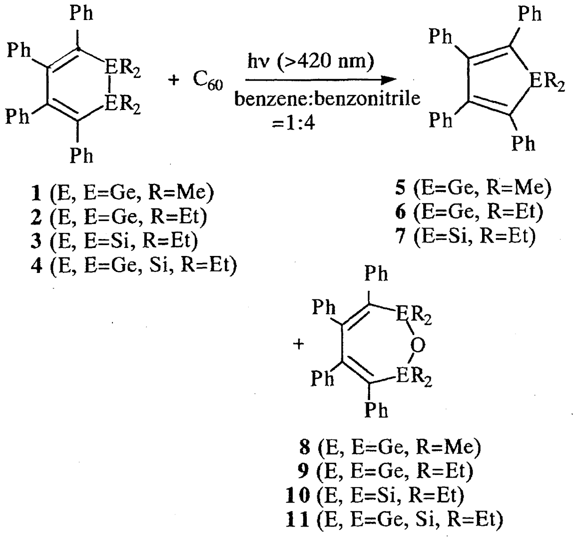
Compound	$\lambda_{\max}$/nm[a)]	E_{th}/eV[b)]
1	330.4	5.17
2	338.0	5.03
3	337.6	5.06
4	338.6	5.32

a) In cyclohexane. b) Retarding-field UPS.

2,7-digermacyclohepta-3,5-diene (**8**) (29%) (Scheme 1). The color of the solution of **1** and C_{60} changed from purple to dark brown during photolysis. Since in the absence of C_{60} no photochemical reaction of **1** occurs at all by irradiation with a sodium lamp, products **5** and **8** should be derived from a photoinduced electron transfer from **1** to C_{60}. The origin of oxygen for **8** is unclear at this moment. In spite of every effort to minimize the moisture and air, **8** was obtained in an appreciable amount.

Products **5** and **8** were isolated in the pure state and characterized by the ^{1}H, ^{13}C NMR and MS spectra in comparison with those of authentic samples.[26)] Product **8** was prepared by the oxidation of **1** with *m*-chloroperbenzoic acid in dichloromethane, and identified by its NMR and MS spectra. The photochemical reactions of 3,4,5,6-tetraphenyl-substituted 1,1,2,2-tetraethyl-1,2-digermacyclohexa-3,5-diene (**2**), 1,1,2,2-tetraethyl-1,2-disilacyclohexa-3,5-diene (**3**), and 1,1,2,2-tetraethyl-1-sila-2-germacyclohexa-3,5-diene (**4**) with C_{60} under similar conditions were also carried out. Upon the irradiation of **2**—**4**, ring-contracted compounds, namely 1-germacyclopenta-2,4-dienes (**6**)[25)] and 1-silacyclopenta-2,4-dienes (**7**),[27)] ring-expanded compounds (**9**—**11**) were formed. All of the photoproducts were verified with the ^{1}H, ^{13}C NMR and GC-MS spectra. The results of the photochemical reactions of **1**—**4** are summarized in Table 2. The ratio of benzene : benzonitrile in solvents did not affect the results in Table 2.

The presence of **5**—**7** suggests the formation of germylenes and silylenes, respectively. From the reactivity of germylenes and silylenes, germylenes and silylenes may be trapped with the carbon–carbon double bonds of C_{60}. UV-vis spectroscopy has been used to obtain such experimental data. The UV-vis spectral change observed in the reaction of **1** and C_{60} in benzene/benzonitrile during photolysis are shown in Fig. 1. The absorbance increases around 440, 550, 625, and 675 nm and decreases around 600 nm. Similar UV-vis spectral behaviors were observed for a photolyzed solution of 7,7-dimethyl-1,2,3,4-tetraphenyl-7-germanorbornadienes as a germylene precursor[28)] in a benzene/benzonitrile solution of C_{60}. Therefore, The UV-vis spectral behaviors given in Fig. 1 may suggest the addition of dimethylgermylene to C_{60}. Ando, Akasaka, and co-workers have reported on a similar UV-vis spectral change in the addition reaction of bis(2,6-diisopropylphenyl)silylene to C_{60}.[20,21)] The photolysis of **4** afforded only 1-silacyclopenta-2,4-diene (**7**), suggesting no generation of diethylsilylene, but that of diethylgermylene, as shown in Table 2. The difference between the photochemical by generated germylenes and silylenes from **4** may be explained by the following reasons. The bond-dissociation energy of a Ge–C bond is less than that of a Si–C bond, and germylenes are virually more thermodynamically stable than silylenes.[29)]



Scheme 1.

Table 2. Results of Photoinduced Electron Transfer from 1,2-Digermacyclohexa-3,5-dienes and Related Compounds **1**—**4** to C_{60}

Compound	Time	Conv.	Products (Yield/%)	
	h	%	Germole (or Silole)	Cyclic oxide
1	10	35	**5** (69)	**8** (29)
2	10	17	**6** (73)	**9** (trace)
3	10	21	**7** (65)	**10** (30)
4	10	23	**7** (54)	**11** (46)

Laser Flash Photolysis Study on Photoinduced Electron-Transfer Process from 1,2-Digermacyclohexa-3,5-dienes and C_{60}. Nanosecond transient absorption spectral measurements were performed on degassed solutions containing 1,2-digermacyclohexa-3,5-diene **1** at 293 K using the second-harmonic pulse of a Nd : YAG laser as the exciting light source. Figure 2 shows the transient absorption spectra obtained by laser irradiation to a degassed solution of benzene : benzonitrile (1 : 5) containing **1** and C_{60}. A transient absorption band at 740 nm is attributed to triplet excited state of C_{60} (${}^{T}C_{60}^{*}$).[30—33)] A small absorption band at 1060 nm can be attributed to an anion radical of C_{60} ($C_{60}^{-\bullet}$).[34,35)] Since the second-harmonic pulse of a Nd : YAG laser excites only C_{60}, the generation of $C_{60}^{-\bullet}$ can be attributed to an electron-transfer reaction from **1** to ${}^{T}C_{60}^{*}$.

$$\mathbf{1} + {}^{T}C_{60}^{*} \rightarrow \mathbf{1}^{+\bullet} + C_{60}^{-\bullet} \qquad (1)$$

Since the absorption-time profile at 1060 nm shows only a gradually rising profile corresponding to the decay of ${}^{T}C_{60}^{*}$, the contribution of the electron-transfer reaction via a singlet excited state of C_{60} (${}^{1}C_{60}^{*}$) to the net ion-radical generation can be neglected under the present experimental conditions. From the result of pulse-radiolysis experiments of **1**, the absorption band of the cation radical of **1** ($\mathbf{1}^{+\bullet}$) is expected to appear at around 390 nm.[36)] Since, however, C_{60} has a strong absorption band at <400 nm, the observation of a transient absorption band of around at 390 nm is difficult. Additionally, the strong absorption of ${}^{T}C_{60}^{*}$ at around 550 and 400 nm makes it difficult to distinguish the absorption band of $\mathbf{1}^{+\bullet}$ from that of ${}^{T}C_{60}^{*}$. Comparing the absorption-time profile at 400 nm with that at 740 nm, the profile at 400 nm shows decay at a slightly slow rate. This slow decay

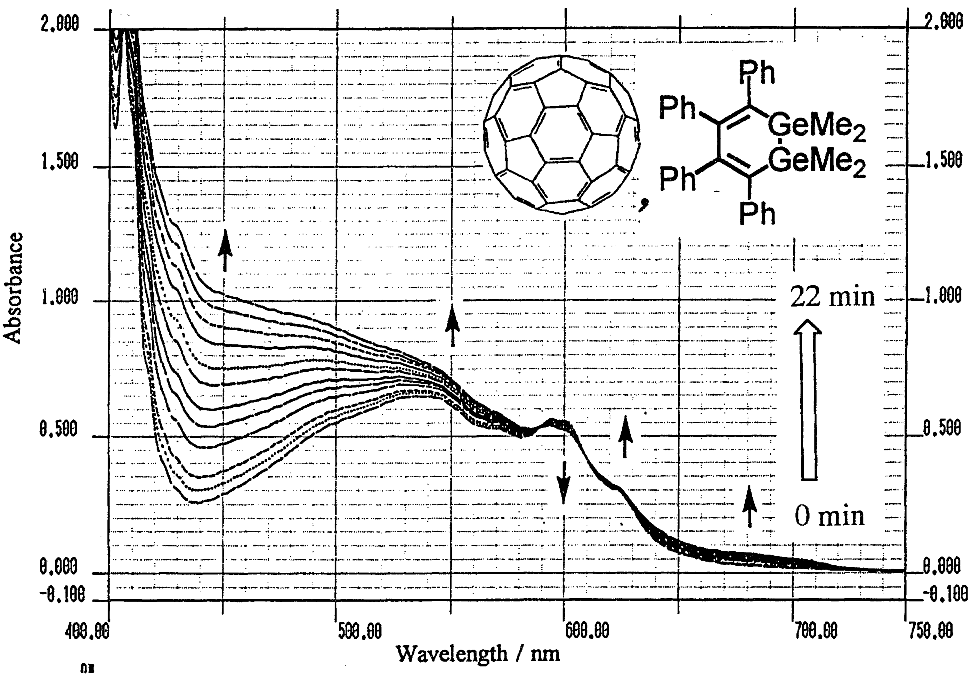


Fig. 1. UV-vis spectral change of C_{60} and **1** in benzene : benzonitrile (1 : 5) during irradiation with a sodium lamp.

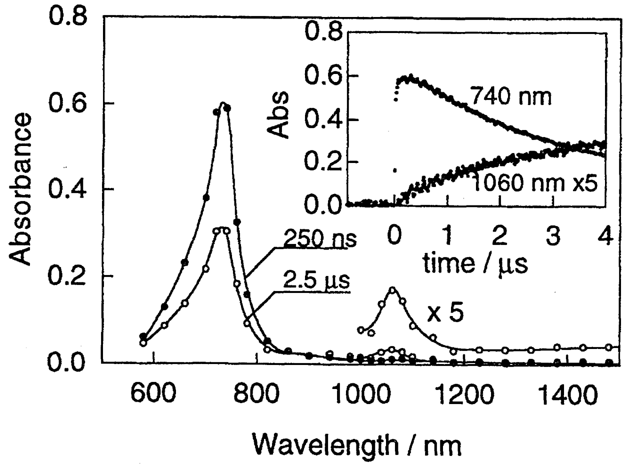


Fig. 2. Transient absorption spectra of 0.2 mM C_{60} and 2 mM **1** in benzene : benzonitrile (1 : 5) mixed solvent. Excitation: SHG (532 nm) of Nd : YAG laser. Insert: Absorption-time profiles at 740 and 1060 nm.

perhaps indicates the existence of a subtle rising component, i.e., the generation of $\mathbf{1}^{+\bullet}$.

The quantum yield (Φ_{et}^{T}) for the generation of $C_{60}^{-\bullet}$ via $^{T}C_{60}^{*}$ can be estimated by using a following relation:

$$\Phi_{et}^{T} = [C_{60}^{-\bullet}]_f/[{}^{T}C_{60}^{*}]_i, \tag{2}$$

where $[C_{60}^{-\bullet}]_f$ and $[{}^{T}C_{60}^{*}]_i$ are the final concentrations of $C_{60}^{-\bullet}$ and $^{T}C_{60}^{*}$, respectively. These concentrations were calculated from the corresponding absorbance at 1060 nm and 740 nm on the basis of the reported extinction coefficient of $C_{60}^{-\bullet}$ (12100 $M^{-1}\,cm^{-1}$)[30] and $^{T}C_{60}^{*}$ (16100 $M^{-1}\,cm^{-1}$) (1 M= 1 $mol\,dm^{-3}$).[32,37] Φ_{et}^{T} is estimated to be 0.076 under the condition described caption on Fig. 2.

The decay rate of $^{T}C_{60}^{*}$ obeys first-order kinetics in the presence of **1**. The decay rate increases with the concentration of **1**, as shown in Fig. 3, in which the slope gives a bimolecular rate constant of 2.42×10^{7} $M^{-1}\,s^{-1}$. From the rise curve of $C_{60}^{-\bullet}$, a similar bimolecular rate constant was evaluated. These bimolecular rate constants clearly correspond to the electron-transfer rate constants.

Solutions containing C_{60} and **1** were very sensitive to laser irradiation, changing from purple to yellow offer only a few ten shots of the laser pulse. In the transient-absorption spectra of the solution which changed to yellow, a new transient absorption band appeared at 700 nm. The new transient absorption band is attributed to the triplet state of the products of the photochemical reaction.

Photoinduced Electron Transfer Mechanism. The

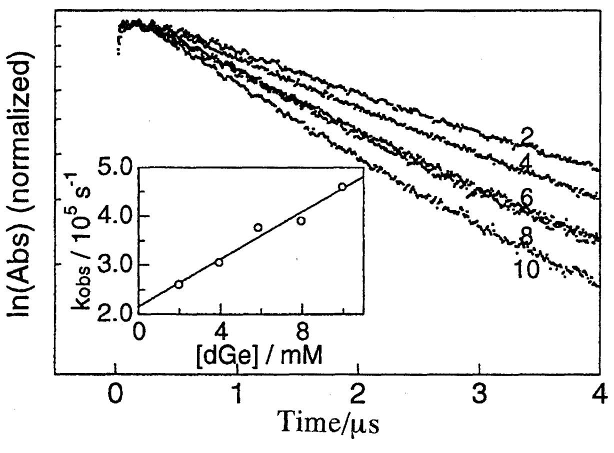


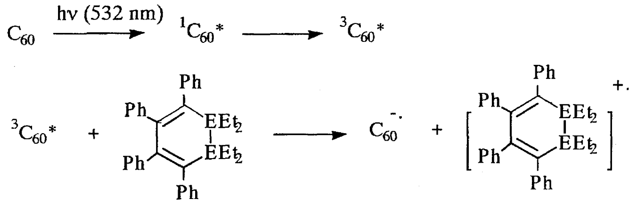
Fig. 3. Absorption-time profiles at 740 nm of 0.2 mM C_{60} and **1** in benzene : benzonitrile (1 : 5) mixed solvent. The number near the profile indicates the concentration of in mM. Insert: The dependence of the first-order rate constant on the concentration of **1**.

results of photochemical reactions and laser flash photolysis studies of 1,2-digermacyclohexa-3,5-dienes and related compounds **1**—**4** are best rationalized as electron transfer from **1**—**4** to photoexcited C_{60}.

Based on the transient absorption spectra and their profiles, the electron transfer takes place via $^3C_{60}^*$ with the photoexcitation of C_{60} by 532 nm light, which is not absorbed by 1,2-digermacyclohexa-3,5-dienes and related compounds, **1**—**4** (Scheme 2). Thus, the electron-transfer reaction from **1** to the photoexcited $^3C_{60}^*$, which is formed by intersystem crossing from $^1C_{60}^*$, takes place to give the corresponding cation radical of **1** and anion radical of C_{60}.[38] The unstable $\mathbf{1}^{+\bullet}$ easily decomposes to the corresponding 1-germa or 1-silacyclopenta-2,4-diene cation radicals along with the release of germylenes or silylenes. The back-electron-transfer reaction of $C_{60}^{-\bullet}$ to 1-germa or 1-silacyclopenta-2,4-diene cation radicals proceeds to give C_{60} and 1-germa or 1-silacyclopenta-2,4-dienes (Scheme 3).

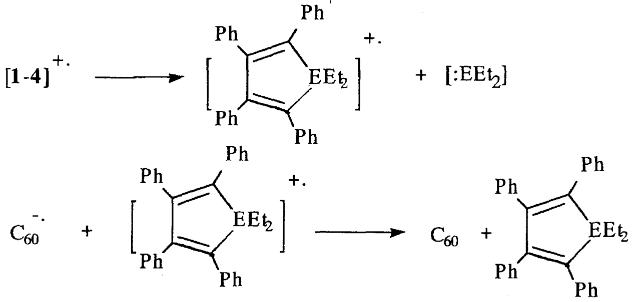
The formation of ring-expanded compounds **8**—**11** is readily explained by the oxygenation of **1**—**4** with singlet oxygen. Singlet oxygen ($^1O_2$) is generated by an energy-transfer reaction between the photoexcited $^3C_{60}^*$ and triplet oxygen ($^3O_2$).[30] Therefore, 1,2-digermacyclohexadiene **1** is subjected to photosensitized oxygenation with $^1O_2$ to afford ring-expanded 1-oxa-2,7-digermacyclopenta-3,5-diene **8**. This is supported by photooxygenation experiments; namely, photolysis of **1** with a trace of rose bengal with a tungsten lamp under oxygen for 3 h gave cyclic oxadigerma compound **8** in ca. 50% yield. A similar photooxygenation of 1,2-disilacyclohexa-3,5-diene with $^1O_2$ has been reported by Sakurai and co-workers.[39]

The formation of cyclic oxadigerma compounds is also accounted for by the oxygenation of the cation radical of 1,2-digermacyclohexadienes with $^3O_2$. This is readily proved by the photolysis of the cation radical $\mathbf{1}^{+\bullet}$, which was generated by the electron transfer of **1** with 9,10-dicyanoanthracene (DCA) as an acceptor[40] in air. This produced the cyclic oxadigerma compound **8** in ca. 50% yield.



1-4 (E, E=Ge, Ge; Si, Si; Ge, Si)

Scheme 2.



Scheme 3.

Experimental

General Methods. All photochemical reactions were carried out in a degassed Pyrex tube. Benzene and benzonitrile were dried and distilled before use. 2,3-Dimethylbuta-1,3-diene was distilled before use. C_{60} was commercially available. The NMR spectra were obtained on a Varian Unity Inova 400-MHz NMR spectrometer. The GC MS spectra were measured on a JEOL JMS-DX 303 mass spectrometer. The UV and UV-vis spectra were recorded on a Shimadzu UV 2200 spectrometer. Gas chromatography was performed on a Shimadzu GC8A with 1 m 20% SE30 column.

Materials. 1,1,2,2-Tetramethyl-3,4,5,6-tetraphenyl-1,2-digermacyclohexa-3,5-diene,[25] 1,1,2,2-tetraethyl-3,4,5,6-tetraphenyl-1,2-digermacyclohexa-3,5-diene,[25] 1,1,2,2-tetraethyl-3,4,5,6-tetraphenyl-1-sila-2-germacyclohexa-3,5-diene,[25] 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene,[41] 1,1-diethyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene,[42] and 1,1-diethyl-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene,[43] were prepared as reported in the literature.

Preparation of 1,1,2,2-Tetraethyl-3,4,5,6-tetraphenyl-1,2-disilacyclohexa-3,5-diene. A mixture of lithium metal (0.5 g, 0.072 mol) and diphenylacetylene (13 g, 0.072 mol) in anhydrous ether was stirred for 16 h at room temperature. To this solution was added anhydrous ether (150 ml), and then 1,2-dichloro-1,1,2,2-tetraethyldisilane (8.7 g, 0.036 mol) in ether (20 ml). After refluxing 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 was evaporated, the residue was diluted with acetone to give pure 1,1,2,2-tetraethyl-3,4,5,6-tetraphenyl-1,2-disilacyclohexa-3,5-diene (3.70 g, 0.007 mol, 21%): Mp 145 °C; ^{1}H NMR (C_6D_6) δ=0.81—0.93 (m, 4H), 1.02—1.12 (m, 4H), 1.17—1.21 (m, 12H), 6.64—7.12 (m, 20H); ^{13}C NMR (C_6D_6) δ=4.84, 9.52, 125.10, 128.83, 127.26, 128.00, 128.93, 130.27, 141.53, 142.45, 142.45, 143.67, 153.49; MS *m/z* 528; UV (cyclohexane) λ_{max} 337.6 nm (log ε 3.49). Anal. Found: C, 82.02; H, 7.52%. Calcd for $C_{36}H_{40}Si_2$: C, 81.76; H, 7.62%.

Preparation of 2,2,7,7-Tetraalkyl-3,4,5,6-tetraphenyl-1-oxa-2,7-digermacyclohepta-3,5-diene and Related Compounds. As a typical example, the preparation of 2,2,7,7-tetramethyl-3,4,5,6-tetraphenyl-1-oxa-2,7-digermacyclohepta-3,5-diene is described. To a solution of 299 mg (0.53 mmol) of **1** in 20 ml of dichloromethane was added a solution of 185 mg (1.1 mmol) of *m*-chloroperbenzoic acid. The mixture was stirred at room temperature for 2 h, during which time the yellow color of **1** disappeared. Recrystallization of the crude product from ethanol gave 2,2,7,7-tetramethyl-3,4,5,6-tetraphenyl-1-oxa-2,7-digermacyclohepta-3,5-diene as oil, 255 mg (97% yield). ^{1}H NMR ($CDCl_3$) δ=0.76 (s, 12H) 6.8—7.5 (m, 20H); ^{13}C NMR ($CDCl_3$) δ=3.7, 120.4, 125.5, 127.6, 129.8, 130.0, 140.7, 143.4, 145.1, 149.4; M$^+$ *m/z* 578 (^{73}Ge); UV (cyclohexane) λ_{max} 280.0 nm (log ε 3.90). 2,2,7,7-Tetraethyl-3,4,5,6-tetraphenyl-1-oxa-2,7-digermacyclohepta-3,5-diene: Mp 146 °C; ^{1}H NMR ($CDCl_3$) δ=1.4—1.7 (m, 10H), 1.7—1.9 (m, 10H), 6.8—7.3 (m, 20H); ^{13}C NMR ($CDCl_3$) δ=7.02, 8.27, 8.50, 10.9, 125.2, 125.9, 127.5, 126.8, 129.8, 140.2, 142.6, 146.4, 152.8; MS *m/z* 634 (^{73}Ge); UV (cyclohexane) λ_{max} 280.0 nm (log ε 4.07). 2,2,7,7-Tetraethyl-3,4,5,6-tetraphenyl-1-oxa-2,7-disilacyclohepta-3,5-diene: Mp 159 °C; ^{1}H NMR ($CDCl_3$) δ=0.3—1.5 (b, 20H), 6.6—7.3 (m, 20H); ^{13}C NMR ($CDCl_3$) δ=5.8—8.0 (m), 124.9, 125.6, 126.7, 127.5, 128.4, 129.7, 140.9, 143.0, 144.2, 154.6; MS *m/z* 544; UV (cyclohexane) λ_{max} 280.0 nm (log ε 4.00). 2,2,7,7-

Tetraethyl-3,4,5,6-tetraphenyl-1-oxa-2-sila-7-germacyclohepta-3,5-diene: Mp 147 °C; ^{1}H NMR ($CDCl_3$) δ =0.33—0.44, 0.50—0.66, 0.66—0.75, 0.80—1.00, 1.04—1.32, 1.33—1.40, 1.50—1.62, 6.6—7.3 (m, 20H); ^{13}C NMR ($CDCl_3$) δ =5.8—6.1, 6.8—7.2, 7.3—7.7, 8.0—8.2, 10.5, 124.5—125.5, 125.6, 125.9, 126.7, 126.8, 127—128, 129.7, 129.9, 140.3, 140.9, 142.3, 143.3, 144.1, 146.5, 153.5, 153.7; MS m/z 590 (^{73}Ge); UV (cyclohexane) $\lambda_{\max}$ 280.0 nm (log ε 4.11).

Photolysis of 1—4 with C_{60}. As a representative example, the photochemical reaction of **1** is described. Benzene–benzonitrile (1 : 4) mixed solutions of 1,2-digermacyclohexa-3,5-diene **1** (10 mM) and C_{60} (1 mM) were adjusted in a Pyrex tube (ϕ =7 mm). The solution was degassed in a vacuum and sealed. The sample was irradiated with a sodium lamp (Ushio Electronic Co., Ltd., JCV100-500 A) for 10 h at room temperature. NMR, GC, and GC-MS analyses of the resulting mixture showed the formation of 1-germacyclopenta-2,4-diene **5** (69%) and cyclic oxadigerma compound **8** (29%).

Photooxygenation of 1 Containing a Trace of Rose Bengal in Acetone under Oxygen. A solution of 20 mg of **1** in 0.7 ml of acetone, containing a trace of Rose bengal, in an NMR tube was irradiated with a sodium lamp under oxygen. The reaction mixture was examined after 3 h, and cyclic oxadigerma compound **8** (ca. 50%) and starting material **1** (50%) were detected by silica-gel TLC, developed with hexane–benzene (4 : 1) and GC-MS.

Photooxygenation of 1 and DCA in CH_2Cl_2 under Oxygen. The irradiation of **1** (11.2 mg) and DCA (0.46 mg) in dichloromethane (2 ml) with a sodium lamp at room temperature for 3 h afforded the cyclic oxadigerma compound **8** in ca. 50% yield. Five milligrams of **1** were recovered.

Time-Resolved Optical Absorption. The nanosecond time-resolved absorption spectra were measured using SHG (532 nm at ca. 30 mJ/pulse) of a Nd : YAG laser (Quanta-Ray, GCR-130, fwhm 6 ns) as the excitation source. A pulsed xenon flash lamp (Tokyo Instruments, XF80-60) was used as the monitoring light. A Ge-APD module (Hamamatsu Photonics, C5331-SPL) was used as the detector for the absorption spectra in the near-IR region (600—1600 nm). The transient-absorption spectra for the visible region were observed by applying a photomultiplier tube (PMT) and a Xe lamp as the detector and monitoring light, respectively. The output signal from the detector was recorded with a digitizing oscilloscope (Hewlett–Packerde 55410B) and analyzed using a personal computer. All of the samples for the laser flash photolysis were contained in a 1 cm quartz cell and were deaerated by 15 min of argon bubbling.

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References

1) J. K. Kochi, "Organometallic Mechanism and Catalysis," Academic Press, New York (1978).

2) V. F. Traven and R. West, *J. Am. Chem. Soc.*, **95**, 6824 (1973).

3) H. Sakurai, M. Kira, and T. Uchida, *J. Am. Chem. Soc.*, **95**, 6826 (1973).

4) K. Mochida, C. Hodota, R. Hata, and S. Fukuzumi, *Organometallics*, **12**, 586 (1993).

5) H. Bock and W. Enssiin, *Angew. Chem.*, **83**, 435 (1971).

6) H. Bock, W. Enssiin, F. Fehner, and R. Freund, *J. Am. Chem. Soc.*, **98**, 668 (1976).

7) C. G. Pitt, M. M. Bursey, and P. F. Rogerson, *J. Am. Chem. Soc.*, **92**, 519 (1970).

8) L. Szepes, T. Koranyi, G. N-Szabo, A. Modelli, and G. Distefano, *J. Organomet. Chem.*, **217**, 35 (1981).

9) K. Mochida, S. D. Worley, and J. K. Kochi, *Bull. Chem. Soc. Jpn.*, **58**, 3389 (1985).

10) K. Mochida, M. Shimoda, H. Kurosu, and A. Kojima, *Polyhedron*, **13**, 3039 (1994).

11) K. Mochida, R. Hata, M. Shimoda, F. Matsumoto, H. Kurosu, A. Kojima, M. Yoshikawa, M. Masuda, and Y. Harada, *Polyhedron*, **15**, 3027 (1996).

12) R. Sension, A. Z. Szarka, G. R. Smith, and R. M. Hochstrasser, *Chem. Phys. Lett.*, **185**, 179 (1991).

13) J. W. Arbogast and C. S. Foote, *J. Am. Chem. Soc.*, **113**, 8886 (1991).

14) J. W. Arbogast, C. S. Foote, and M. Kao, *J. Am. Chem. Soc.*, **114**, 2277 (1992).

15) L. Biczok and H. Linschitz, *Chem. Phys. Lett.*, **195**, 339 (1992).

16) T. Osaki, Y. Tai, M. Tazawa, S. Tanemura, K. Inukawa, K. Ishiguro, Y. Sawaki, Y. Saito, H. Shinohara, and H. Nagashima, *Chem. Lett.*, **1993**, 789.

17) S. Nonell, J. W. Arbogast, and C. S. Foote, *J. Phys. Chem.*, **96**, 4169 (1992).

18) D. M. Guldi, H. Hungerbuhler, E. Janata, and K.-D. Asmus, *J. Chem. Soc., Chem. Commun.*, **1993**, 84.

19) H. Ghosh, H. Pal, A. V. Sapre, and J. P. Mittal, *J. Am. Chem. Soc.*, **115**, 11722 (1993).

20) T. Akasaka, W. Ando, K. Kobayashi, and S. Nagase, *J. Am. Chem. Soc.*, **115**, 1605 (1993).

21) T. Akasaka, W. Ando, K. Kobayashi, and S. Nagase, *J. Am. Chem. Soc.*, **115**, 10366 (1993).

22) X. Zhang, A. Romero, and C. Foote, *J. Am. Chem. Soc.*, **115**, 11024 (1993).

23) Y. Nakadaira, S. Kanouchi, and H. Sakurai, *J. Am. Chem. Soc.*, **96**, 5623 (1974).

24) H. Sakurai, Y. Nakadaira, and H. Tobita, *Chem. Lett.*, **1982**, 1855.

25) K. Mochida, M. Akazawa, T. Kayamori, A. Sekine, Y. Ohhashi, M. Kako, and Y. Nakadaira, *Organometallics*, to be published.

26) P. Jutzi and A. Kari, *J. Organomet. Chem.*, **215**, 19 (1981).

27) B. Resibois, C. Hode, B. Picart, and J. C. Brunet, *Ann. Chim.*, **4**, 203 (1969).

28) W. P. Neumann, *Chem. Rev.*, **91**, 311 (1991).

29) K. M. Mackay, "The Chemistry of Organic Germanium, Tin, and Lead Compounds," ed by S. Patai, John Wiley & Sons, New York (1995), Chap. 2.

30) J. W. Arbogast, A. P. Darmanyan, C. S. Foote, Y. Rubin, F. N. Diederich, M. M. Alvarez, S. J. Anz, and R. L. Whetten, *J. Phys. Chem.*, **95**, 11 (1991).

31) Y. Kajii, T. Nakagawa, S. Suzuki, Y. Achiba, K. Obi, and K. Shibuya, *Chem. Phys. Lett.*, **181**, 100 (1991).

32) R. J. Sension, C. M. Phillips, A. Z. Szarka, W. J. Romanow, A. R. Macghie, J. P. McCauley, A. B. Smith, III, and R. M. Hochstrasser, *J. Phys. Chem.*, **95**, 6075 (1991).

33) N. M. Dimitrijevic and P. V. Kamat, *J. Phys. Chem.*, **96**, 4811 (1992).

34) T. Kato, T. Kodama, T. Shida, T. Nakagawa, Y. Matsui, S. Suzuki, H. Shiromaru, K. Yamauchi, and Y. Achiba, *Chem. Phys. Lett.*, **180**, 446 (1991).

35) Z. Gasyna, L. Andrews, and P. N. Schatz, *J. Phys. Chem.*,

96, 1525 (1992).

36) Radical cation of **1** was generated by using linear accelerator system (LINAC) (28 MeV single electron beam, 2 ns pulse width). The transition absorption spectra of $\mathbf{1}^{+\bullet}$ in CH_2Cl_2 solution appeared at 390 nm.

37) O. Ito and A. Watanabe, "Fullerenes," ed by R. O. Ruoff and K. M. Kadish, Electrochemical Society, 1996, p. 297.

38) a) A. Watanabe, O. Ito, M. Watanabe, H. Saito, and M. Koishi, *J. Chem. Soc., Chem. Commun.*, **1996**, 117; b) A. Watanabe, O. Ito, and K. Mochida, *Organometallics*, **14**, 4281 (1995); c) O. Ito, Y. Sasaki, A. Watanabe, and K. Mochida, *Bull. Chem. Soc. Jpn.*, **69**, 2167 (1996).

39) Y. Nakadaira and H. Sakurai, *J. Organomet. Chem.*, **47**, 61 (1973).

40) For example: Y. Nakadaira, A. Sekiguchi, Y. Funada, and H. Sakurai, *Chem. Lett.*, **1991**, 327.

41) N. K. Hota and C. J. Willis, *J. Organomet. Chem.*, **15**, 84 (1968).

42) P. Jutzi and A. Kari, *J. Organomet. Chem.*, **215**, 19 (1981).

43) B. Resibois, C. Hode, B. Picart, and J. C. Brunet, *Ann. Chim.*, **4**, 203 (1969).