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A First Photochemical Bis-germylation of C_{60} with Digermirane

Takeshi Akasaka,[*,†,‡] Yutaka Maeda,[†] Takatsugu Wakahara,[†] Takashi Mizushima,[§] Wataru Ando,[§] Markus Wälchli,[‖] Toshiyasu Suzuki,[‡] Kaoru Kobayashi,[⊥] Shigeru Nagase,[⊥] Masahiro Kako,[#] Yasuhiro Nakadaira,[#] Mamoru Fujitsuka,[▼] Osamu Ito,[▼] Yoshiko Sasaki,[★] Kazunori Yamamoto,[♦] and Tomoki Erata[■]

Graduate School of Science and Technology, Niigata University, Niigata 950-2181, Japan, Institute for Molecular Science, Okazaki 444-8585, Japan, Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan, Bruker Japan Co., Ltd., Tsukuba, Ibaraki 305-0051, Japan, Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Tokyo 192-0397, Japan, Department of Applied Physics and Chemistry, The University of Electro-communications, Tokyo 182-8585, Japan, Institute for Chemical Reaction Science, Tohoku University, Sendai, 980-8577, Japan, Shokei Girl's High Schools, Aoba-ku, Sendai 980-0873, Japan, Tokai Works, Power Reactor and Nuclear Fuel Development Corporation, Tokai, Ibaraki 319-1100, Japan, and Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

akasaka@gs.niigata-u.ac.jp

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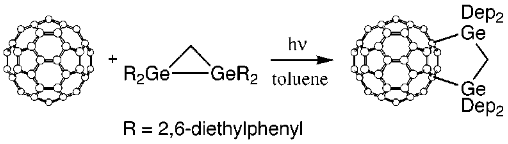
ABSTRACT



In the photochemical bis-germylation of C_{60} with 1,1,2,2-tetrakis(2,6-diethylphenyl)-1,2-digermirane (1), a cycloadduct (2) is obtained in high yield for the first time. Spectroscopic analysis and theoretical investigation confirm that 2 (which has C_1 symmetry) results from 1,4-cycloaddition. Control experiments and laser flash photolysis experiments suggest that an exciplex intermediate is responsible for the formation of 2. The redox properties of 2 were examined by differential pulse voltammetry.

Numerous fullerene chemical transformations have been developed since the isolation of C_{60} in preparatively useful quantities.[1] Among the various reactions to be used for functionalization of C_{60}, cycloaddition reactions[2,3] have been successfully employed for the preparation of ring-fused C_{60} derivatives.[1] It has been found that photoexcited C_{60} is a strong electron acceptor[4] and strained Si−Si[5] and Ge−Ge[6] σ bonds can act as an electron donor. We have recently

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[†] Niigata University.
[‡] Institute for Molecular Science.
[§] University of Tsukuba.
[‖] Bruker Japan Co., Ltd.
[⊥] Tokyo Metropolitan University.
[#] The University of Electro-communications.
[▼] Tohoku University.
[★] Shokei Girl's High Schools.
[♦] Tokai Works, Power Reactor and Nuclear Fuel Development Corporation.
[■] Hokkaido University.

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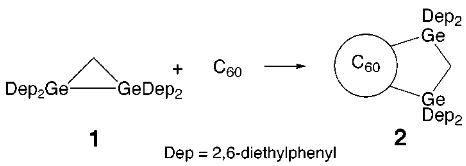
reported that the photochemical cycloaddition of C_{60} with a disilirane takes place to afford 1,2-cycloadduct via the intermediacy of an exciplex.[2b,7] We report here the novel photochemical bis-germylation of C_{60} with a digermirane as the first example of 1,4-cycloaddition, which would lead to a new route to synthetically useful bis-germylation chemistry.

Irradiation of a degassed toluene solution of 1,1,2,2-tetrakis(2,6-diethylphenyl)-1,2-digermirane[8] (**1**, 3.3×10^{-3}M) and C_{60} (3.3×10^{-3}M) with a high-pressure mercury-arc lamp (cutoff <300 nm) resulted in formation of the bis-germylated cycloadduct (**2**)[9] quantitatively with complete consumption of C_{60} (Scheme 1). Pure **2** can be readily isolated in 61% yield by preparative HPLC. The digermirane was thermally unreactive toward C_{60} at 100 °C.[10]

Scheme 1



FAB mass spectrometry of **2** ($C_{101}H_{54}Ge_2$) displays a peak for **2** at *m/z* 1416−1412 as well as a C_{60} peak at *m/z* 723−720 which arises from loss of **1**.

The ^{1}H NMR spectrum of **2** displays eight methyl signals at 1.54, 1.31, 0.87, 0.78, 0.77, 0.71, 0.54, and 0.50 ppm and 16 methylene signals on the ethyl groups between 4.2 and 2.4 ppm. An AB quartet ($J = 14.3$ Hz) for the two methylene protons was also observed at 2.60 and 2.40 ppm. In the H−H COSY NMR spectrum, two cross-peaks corresponding to the methylene protons were observed at 2.60 and 2.40 ppm. The resolved 125 MHz ^{13}C NMR spectrum showed the C_{60} adduct resonances which are expected for a C_1-symmetrical compound. Except for the two bridgehead resonances at 66.2 and 65.9 ppm, all fullerene ^{13}C NMR signals appeared in the spectral range between 165 and 135 ppm. In the H−C COSY NMR spectrum, two cross-peaks corresponding to the methylene protons at 2.60 and 2.40 ppm and one cross-peak due to the methylene carbon atom of the digermirane component at 19.4 ppm were observed. These spectral data suggest that the cycloadduct **2** has C_1 symmetry. As is apparent from the consideration of molecular modeling, **2** must result from either 1,2-cycloaddition or 1,4-cycloaddition.

In the INADEQUATE (Incredible Natural Abundance Double Quantum Experiment) NMR spectrum of **2** obtained from carbon-13-enriched (10%) C_{60}, a cross-peak corresponding to two sp^3 carbon atoms of the fullerene skeleton was not observed at 66.2 and 65.9 ppm, indicating that there is no connectivity between them. As shown in Figure 1, each of the sp^3 carbon atoms has three cross-peaks associated with the sp^2 carbon atoms of the fullerene component. These results clearly reveal that **2** results from 1,4-cycloaddition.[11]

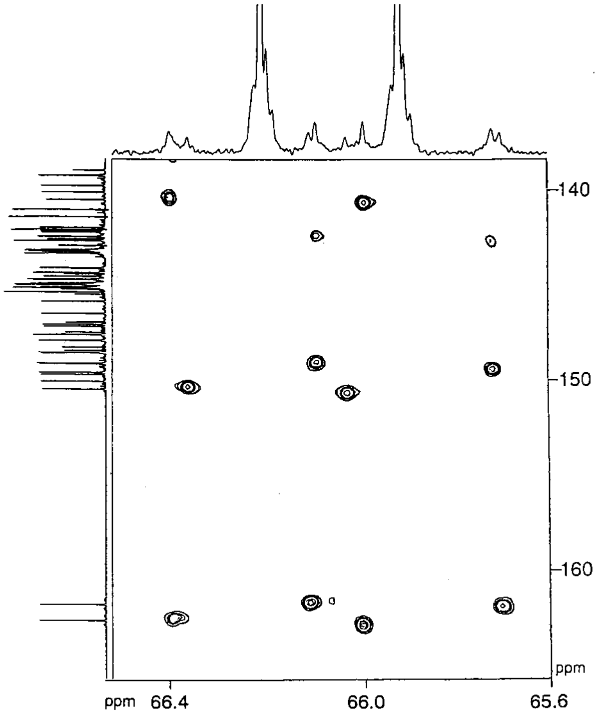


Figure 1. Expansion of the 125 MHz INADEQUATE NMR spectrum of **2**.

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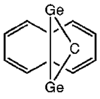
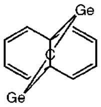
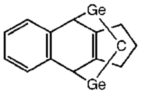
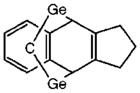
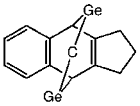
Table 1. Relative Energies (kcal/mol) of Isomers of **2**

1,2-addition		1,4-addition		
envelope-form	twist-form	5-membered envelope-form	6-membered envelope-form	twist-form
 **a** (C_s)	 **b** (C_2)	 **c** (C_s)	 **d** (C_s)	 **e** (C_1)
1.2	4.4	2.8	3.2	0.0

As Table 1 shows, full geometry optimization was carried out for the 1,2-cycloadducts (**a** and **b**) and 1,4-cycloadducts (**c**, **d**, and **e**) at the AM1 level.[12] The 1,2-adducts are less stable than the 1,4-cycloadducts, and have C_s (**a**) and C_2 (**b**) symmetry (not C_1 symmetry). It is notable that the most stable is the structure (**e**) resulting from 1,4-cycloaddition which has C_1 symmetry in the twisted form. This agrees with the experimental finding from spectroscopic data. The optimized structure of **e** is shown in Figure 2. Analysis of the HC three-bond coupling in the gradient HMBC NMR spectrum, which is associated with the dihedral angles between the methylene protons and the sp^3 carbon atoms, gave crucial evidence for the twisted form, as shown in Figure 3. For **e** one proton of a methylene group couples with one sp^3 carbon atom and another proton couples to another sp^3 carbon atom, whereas, for **c** and **d**, one proton of a methylene group couples with two sp^3 carbon atoms of the fullerene skeleton and another proton does not couple with any sp^3 carbon atom. In Figure 3, two cross-peaks corresponding to a proton of the methylene group at 2.60 ppm and a sp^3 carbon atom at 65.9 ppm, and a proton at 2.40 ppm and a carbon atom at 66.2 ppm, respectively, were actually observed. Coalescence of the methyl signals at 0.87 and 0.78 ppm at 75 °C reflecting conformational change of the molecule was observed, yielding an activation energy $\Delta G^{\ddagger} = 17.8$ kcal/mol.[13] This high barrier is ascribed to the fact that the space between C_{60} and 2,6-diethylphenyl groups as well as between 2,6-diethylphenyl groups becomes filled upon transformation from one twist-conformer to the other.

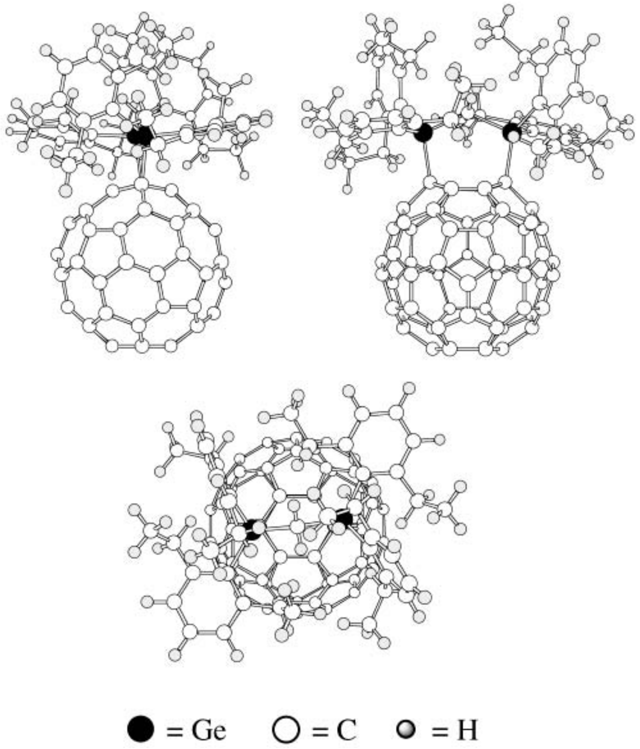


Figure 2. Three views of the twisted C_1 structure (**e**) of **2** optimized with the AM1 method.

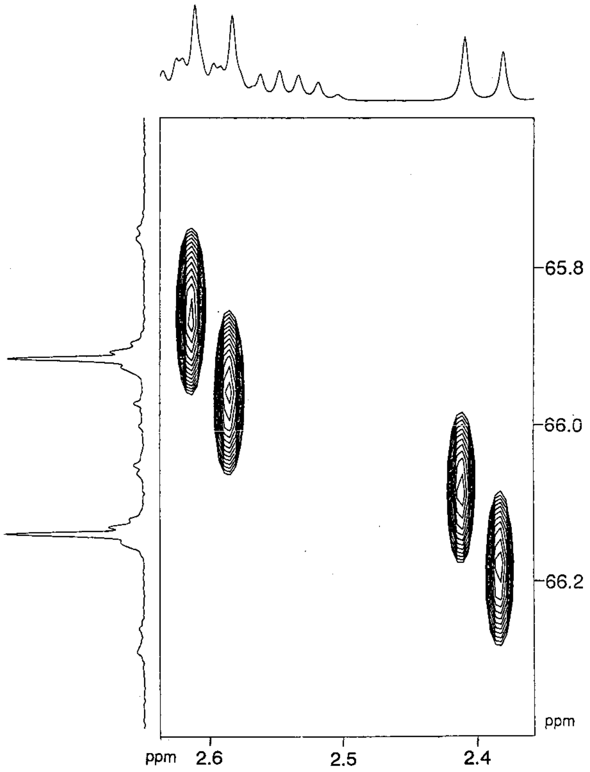


Figure 3. Expansion of the HMBC NMR spectrum of **2**.

The redox properties of **2** were examined by cyclic (CV) and differential pulse (DPV) voltammetries.[14] Table 2 shows the redox potentials of carbon- (**3**),[14] silicon- (**4**),[14] and germanium-containing (**2**) organofullerenes. The electron affinities of these organofullerenes decrease in the order **3** > **2** > **4**, which is in accord with the electronegativity order of the attached atoms. This is in agreement with the

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[13] $\Delta G^{\ddagger}$ values were calculated according to the Eyring equation.

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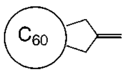
Table 2. Redox Potentials of C_{60}, **2**, **3**, and **4**[a]

compd	${}^{ox}E2$	${}^{ox}E1$	${}^{red}E1$	${}^{red}E2$	${}^{red}E3$
C_{60}		$+1.26^{b,c}$	-1.13	-1.50	-1.95
2	$+1.27^{b,c}$	$+0.59^{b,c}$	-1.24	-1.63	-2.15
3		$+1.03^{b,c}$	-1.23	-1.58	-2.11
4	$+1.22^{b,c}$	$+0.60^{b,c}$	-1.29	-1.67	-2.18

[a] Half-cell potentials unless otherwise stated. Values are in volts relative to ferrocene/ferrocenium couple. Conditions: 0.1 M $(n\text{-Bu})_4NPF_6$ in 1,2-dichlorobenzene; working electrode, Pt disk (1-mm diameter); counter electrode, Pt wire; reference electrode, Ag/0.01 M $AgNO_3$ and 0.1 M $(n\text{-Bu})_4NClO_4$ in CH_3CN. CV: scan rate, 20 mV/s. [b] Irreversible. [c] Values were obtained by DPV: pulse amplitude, 50 mV; pulse width, 50 ms; pulse period, 200 ms; scan rate, 20 mV/s.



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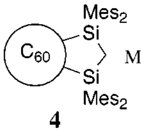

4

Mes = mesityl

calculations which indicate that the LUMO levels increase in the order **3** (−2.80 eV) < **2** (−2.59 ev) < **4** (−2.49 ev). Interestingly, **2** shows two oxidation peaks by DPV as previously observed for **4**.[14] The salient feature in Table 2 is that **2** has a remarkably low oxidation potential (+0.59 V vs Fc/Fc+ couple), as does **4** (+0.60 V), compared to the value of **3** (+1.03 V). This result is in agreement with the fact that the HOMO levels of **2** (−8.73 eV) and **4** (−8.68 ev) are higher than that of **3** (−9.24 eV). It may thus be assumed that partial charge transfer into C_{60} from the germanium group in **2** occurs, as in the case of **4**.[14]

The free energy change (ΔG) for electron transfer from **1** to the triplet state of C_{60} is 6.0 kcal/mol.[4a,15] Consumption of **1** was suppressed by addition of 10 equiv of diazabicyclo[2.2.2]octane (Ep = 0.70 V vs SCE)[16] and 100 equiv of 1,2,4,5-tetramethoxybenzene (Ep = 0.79 V vs SCE),[16] each of which has a low oxidation potential as well as **1** and is unreactive to photoreaction of C_{60}. No absorption is observed at $\lambda > 400$ nm for **1**. The photochemical cycloaddition smoothly proceeds upon irradiation at $\lambda > 400$ nm where C_{60} is the only light-absorbing component. One plausible rationale for these observations is that an exciplex intermediate derived from **1** and the triplet state of C_{60} may be responsible for formation of **2**.[2b] The transient absorption band at 740 nm due to ${}^3C_{60}{}^*$ in benzene obtained by 532 nm laser photolysis of C_{60} decays in the presence of digermirane **1** without generation of C_{60} anion radical at 1070 nm.[7,17] The decay rates of the transient absorption band of ${}^3C_{60}{}^*$ increase with concentration of **1**. These results may suggest the exciplex formation between **1** and ${}^3C_{60}{}^*$ as occurs for the case of disilirane.[7]

Acknowledgment. This work was supported in part by the Asahi Glass Foundation and by a Grant-in-Aid from the Ministry of Education, Science, Sports, and Culture of Japan.

Supporting Information Available: Detailed procedures for the preparation of **2**, complete spectroscopic characterization of **2**, CV and DPV voltammograms, computer-generated models of **2**, and transient absorption spectra obtained by laser flash photolysis of C_{60} with **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The ΔG value was calculated according to the Rehm−Weller equation[18] ($\Delta G = 23.06[E(D/D^+) - E(A^-/A) - \Delta E_{0,0} + 0.74^{19}]$), by using the oxidation potential of **1** (0.72 V vs SCE),[8b] the reduction potential of C_{60} (−0.36 V vs SCE),[20] and the triplet enrgy of C_{60} (1.56 V).[21]

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(19) Coulombic interaction energy in toluene: 0.74 was calculated according to the literature method.[22]

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