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Novel Metal-Free Bis-silylation: C_{60}-Sensitized Reaction of Disilirane with Benzonitrile

Takeshi Akasaka,*[†,‡] Yutaka Maeda,[†] Takatsugu Wakahara,[†] Mutsuo Okamura,[†] Mamoru Fujitsuka,[§] Osamu Ito,[§] Kaoru Kobayashi,[||] Shigeru Nagase,[||] Masahiro Kako,[⊥] Yasuhiro Nakadaira,[⊥] and Ernst Horn[#]

Graduate School of Science and Technology, Niigata University, Niigata 950-2181, Japan, Institute for Molecular Science, Okazaki 444-8585, Japan, Institute for Chemical Reaction Science, Tohoku University, Sendai, 980-8577, Japan, Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan, Department of Chemistry, The University of Electro-Communications, Chofu, Tokyo 182−8585, Japan, and Department of Chemistry, RIKKYO University, Tosima-ku, Tokyo 171-8501, Japan

akasaka@gs.niigata-u.ac.jp

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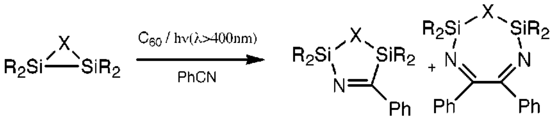
ABSTRACT



The photochemical reaction of disilirane with C_{60} in benzonitrile affords the adduct of disilirane and benzonitrile as a bis-silylated product. In this reaction, C_{60} serves as a sensitizer. The results are reasonably accounted for by a novel metal-free bis-silylation of an unsaturated compound via a photoinduced electron-transfer process.

Much attention has been focused on the photoinduced electron-transfer reaction of group 14 organometallic compounds[1] in which, for example, a Si−Si σ bond can act as a good electron donor.[2] The cation radicals produced in the photoinduced electron transfer of disilane derivatives can be efficiently trapped with polar solvents such as alcohol.[3] Although a number of "mono-silylation" reactions of olefinic and aromatic compounds using organosilicon radical cations have appeared in the literature,[1,2] there has been no example of "bis-silylation" under such conditions. Bis-silylation of unsaturated organic compounds has long attracted special interest in the area of organic synthesis because it could introduce two silicon groups in one molecule simultaneously.[4,5] Up to now, the success in bis-silylation has been limited to transition metal complex-mediated systems. C_{60}

[†] Niigata University.
[‡] Institute for Molecular Science.
[§] Tohoku University.
[⊥] Tokyo Metropolitan University.
[||] The University of Electro-Communications.
[#] RIKKYO University.

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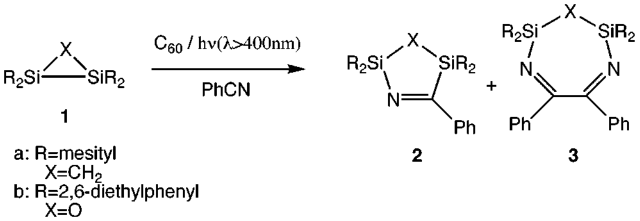
serves as a new electron acceptor and moreover photoexcited C_{60} is an excellent acceptor in electron-transfer processes.[6−12] We already reported the first photochemical bis-silylation of C_{60} with disilirane **1**[13] to afford the 1:1 adduct *in nonpolar solvent*.[14] We herein report a novel metal-free bis-silylation[15] of benzonitrile by the photoreaction of C_{60} with **1** via a photoinduced electron transfer *in polar solvent*, which would lead to a new route to synthetically useful bis-silylation chemistry.

Irradiation of a benzonitrile solution of disilirane **1a** (5×10^{-4} M) and C_{60} (5×10^{-4} M) with a tungsten−halogen lamp using a sodium nitrite filter solution (cutoff <400 nm) resulted in formation of the 1:1 (**2a**) and 1:2 adducts (**3a**) of **1a** and benzonitrile in good yields instead of the adduct of **1a** with C_{60}[14] (Scheme 1). The 1:1 adduct (**2b**) of oxadisilirane (**1b**) with benzonitrile was also obtained under similar reaction conditions. The structures of **2a**, **2b**, and **3a** were characterized by the spectroscopic data, and those for **2b** and **3a** were finally determined by X-ray crystallographic analysis[16] (Figure 1).

Scheme 1



Disilirane **1a** and **1b** have no absorptions at wavelengths over 350 nm, which allows irradiation for excitation of C_{60} only at wavelengths longer than 400 nm. The free energy change (ΔG) for electron transfer from **1a** to the triplet state of C_{60} in benzonitrile is −7.8 kcal/mol.[17,18] Formation of **2a** and **3a** was suppressed by addition of diazabicyclo[2.2.2]-octane and 1,2,4,5-tetramethoxybenzene, each of which has

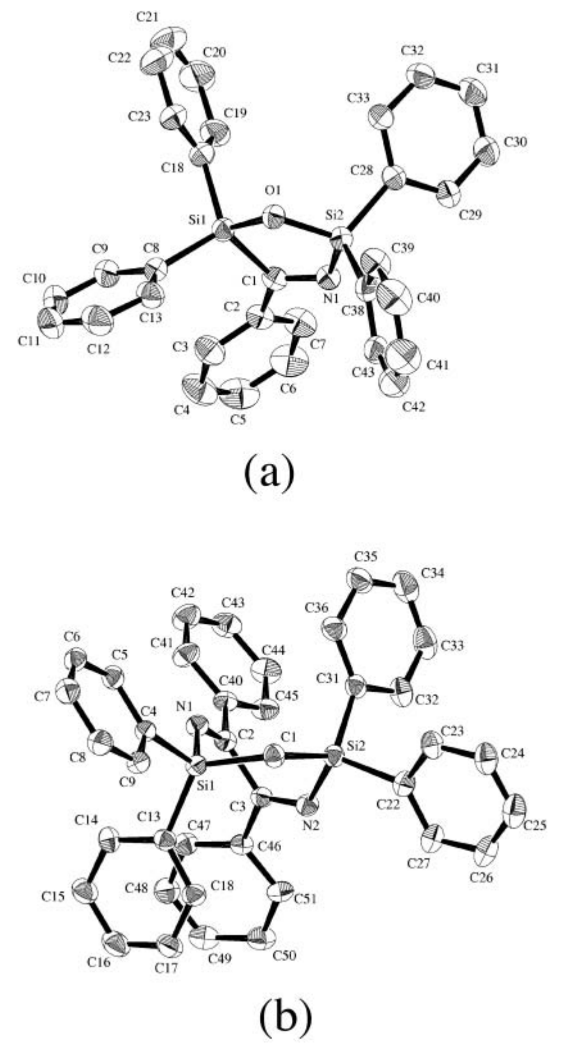


Figure 1. ORTEP views of (a) **2b** and (b) **3a**, showing only selected non-hydrogen atoms for clarity. Thermal ellipsoids are shown at 30% probability level. Selected bond distances (Å) and bond angles (deg) of **2b**: Si(1)−N(1) 1.766(5); Si(1)−C(1) 1.888(6); Si(2)−N(2) 1.755(5); Si(2)−C(1) 1.901(6), N(1)−Si(1)−C(1) 102.7(2); N(1)−Si(1)−C(4) 112.3(3). For **3a**: Si(1)−O(1) 1.656(3); Si(2)−O(1) 1.654(3); Si(1)−C(1) 1.941(4); Si(2)−N(1) 1.764(3); N(1)−C(1) 1.281(5), O(1)−Si(1)−C(1) 94.0(2); O(1)−Si(2)−N(1) 99.9(1); Si(1)-O(1)−Si(2) 116.5(2); Si(1)−C(1)−N(1) 115.2(3); Si(2)−N(1)−C(1) 115.2.

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[16] In the case of 1,1,2,2-tetrakis(2,6-diethylphenyl)-1,2-disilirane, the 1:1 adduct of the disilirane and benzonitrile was also produced; however, the 1: 2 adduct not detected as well as in the case of **1b**.

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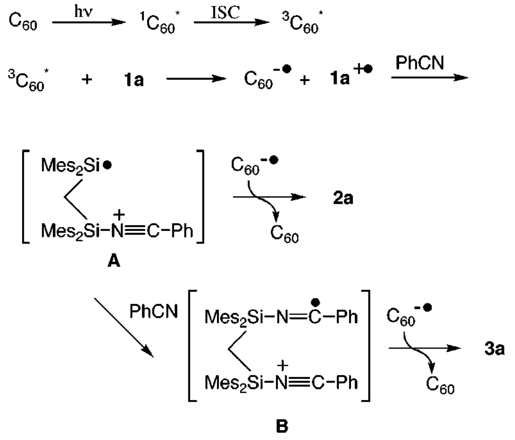
[18] The ΔG value was calculated according to the Rehm−Weller equation[17] ($\Delta G = 23.06[E(D/D^+) - E(A/A^-) - \Delta E_{0,0} - 0.03]$) by using the oxidation potential of **1a** (0.27 V), the reduction potential of C_{60} (−0.98 V), and the triplet energy of C_{60} (1.56 V).[6a] Cyclic voltammogram values of **1a** and C_{60} were in volts relative to the ferrocene/fellocenium couple. Conditions: 0.1 M $(n\text{-Bu})_4NPF_6$ in benzonitrile; working electrode, Pt disk (1-mm diameter); counter electrode, Pt wire; reference electrode, SCE (for **1a**); Ag/0.01 M $AgNO_3$ and 0.1 M $(n\text{-Bu})_4NClO_4$ in acetonitrile (for C_{60}). CV: scan rate, 20 mV/s. Coulombic interaction energy in benzonitrile, −0.03, was calculated according to the literature method.[18a,b] (a) Mattay, J.; Runsink, J.; Rumbach, T.; Cuong, L.; Gersdorf, J. *J. Am. Chem. Soc*. **1985**, *107*, 2557. (b) Mattay, J.; Runsink, J.; Gersdorf, J.; Rumbach, T.; Cuong, L. *Helv. Chem. Acta* **1986**, *69*, 442.

a lower oxidation potential than that of **1a** and is unreactive toward C_{60}.[14] These results suggest one plausible rationale for formation of cycloadducts, **2a** and **3a**, in which an electron transfer from **1a** to $^3C_{60}$* takes place, as shown in Scheme 2. Photochemically generated reactive cation radical **1a**$^{+\bullet}$ could be efficiently captured with benzonitrile acting as a nucleophile to afford intermediate **A**, followed by addition of benzonitrile to produce **B**. Then, **2a** and **3a** are formed by coupling of the resulting biradical intermediate via a back electron transfer process (Scheme 2). AM1 MO calculations[19] show that **1a**$^{+\bullet}$ corresponds to a local minimum on the potential energy surface. This is also confirmed by nonlocal hybrid density functional calculations at the B3LYP/6-311G(d,p) level for parent cation radical **1c**$^{+\bullet}$ (R = H, X = CH_2).[19]

Scheme 2



A remarkable solvent effect observed in the photoinduced electron-transfer reaction of disilirane **1** with C_{60} differentiates the product formation. The photoinduced electron-transfer reactions of C_{60} have been extensively investigated by photochemical techniques such as a laser flash photolysis.[6a,20] To shed light on the mechanism of the reaction of **1a** with C_{60}, 532 nm laser photolysis was carried out to observe transient absorption bands in the near-IR region.[21] In benzene, the absorption band of $C_{60}^{-\bullet}$, which would be anticipated to appear at 1070 nm, was not observed at all, although the decay of $^3C_{60}$* at 740 nm was accelerated, probably due to the generation of an exciplex intermediate followed by the formation of the adduct of **1a** and C_{60}[10] (Figure 2a). In benzonitrile, the absorption band of $^3C_{60}$* at 740 nm, which was immediately observed after the laser exposure, began to decay in the presence of **1a** (Figure 2b). Accompanying the decay of $^3C_{60}$* at 740 nm, the absorption intensity of $C_{60}^{-\bullet}$ at 1070 nm increased, reaching a saturated intensity after about 500 ns.[21] Thus, it is evident that $^3C_{60}$* plays an important role in these reactions to afford $C_{60}^{-\bullet}$ by an electron transfer from **1a**. These results also indicate that the formation of **2** should be rationalized in terms of the intermediacy of **1**$^{+\bullet}$ generated by an electron transfer from **1** to $^3C_{60}$*. This electron-transfer mechanism is further substantiated by the formation of **2a** and **3a** in the photoreaction of **1a** in the presence of a catalytic amount of C_{60}, in which C_{60} acts as an electron-transfer sensitizer. Similar results were also obtained by using a small amount of C_{70}, 9,10-dicyanoanthracene, and 2,4,6-triphenylpyrylium tetrafluoroborate as sensitizers.

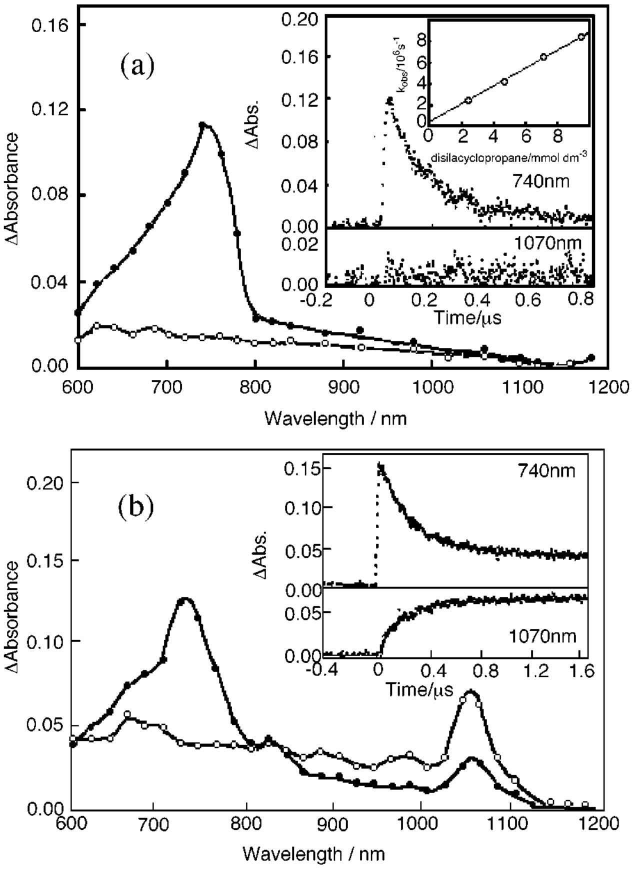


Figure 2. Transient absorption spectra obtained by 532-nm laser flash photolysis of C_{60} (0.1 mM) in the presence of disilirane **1a** (2.5 mM) (a) in deaerated benzene: (●) 50 ns and (○) 500 ns. Inset: time profiles at 740 and 1070 nm and pseudo-first-order plots for the decay of $^3C_{60}$* at 740 nm in the presence of **1a**. (b) In deaerated benzonitrile: (●) 100 ns and (○) 1 μs. Inset: time profiles at 740 and 1070 nm.

In conclusion, a photoinduced electron-transfer bis-sily-

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(19) The AM1[19a] and B3LYP[19b] calculations were carried out using the Gaussian 94 program: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, 1995. (a) Dewar, M. J. S.; Jie, C. X. *Organometallics* **1987**, *6*, 486. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

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lation is noteworthy because it can proceed under mild condition without a metal catalyst.

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Supporting Information Available: Detailed procedures for the preparation and complete spectroscopic characterization of **2a**, **2b**, and **3a**, complete X-ray structure reports for **2b** and **3a**, the AM1-optimized structures of **1a** and **1a**$^{+\bullet}$, and the charge and spin densities of **1a**$^{+\bullet}$ at the HF/3-21G//AM1 level. This material is available free of charge via the Internet at http://pubs.acs.org.

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