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C_{60}-sensitized bis-silylation of nitrile and carbonyl compounds with disilirane

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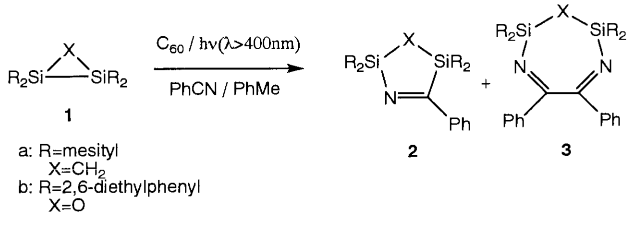
Abstract

The photochemical reaction of disilirane with unsaturated compounds such as nitrile, ketone and aldehyde in the presence of C_{60} with a halogen lamp (cutoff <400 nm) affords the corresponding adducts of disilirane and unsaturated compounds as bis-silylated products. The experimental results by using laser flash photolysis technique confirm the formation of the adducts via a photoinduced electron transfer process between **1** and $^3C_{60}^*$. In this bis-silylation reaction, C_{60} serves as a sensitizer. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Disilirane; Photoinduced electron transfer; Radical ion pair; C_{60}; C_{60}-sensitization

1. Introduction

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 [1,3], 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]. Up to now, the success in bis-silylation has been limited to transition metal complex-mediated systems. C_{60} serves as a new electron acceptor and moreover photoexcited C_{60} is an excellent acceptor in electron transfer processes [5–11]. We have already reported the first photochemical bis-silylation of C_{60} with disilirane **1** [12] to afford the 1:1 adduct *in nonpolar solvent* [13]. Very recently, we have found the formation of the benzonitrile adducts of **1** in benzonitrile [14]. We herein report a novel metal-free



Scheme 1.

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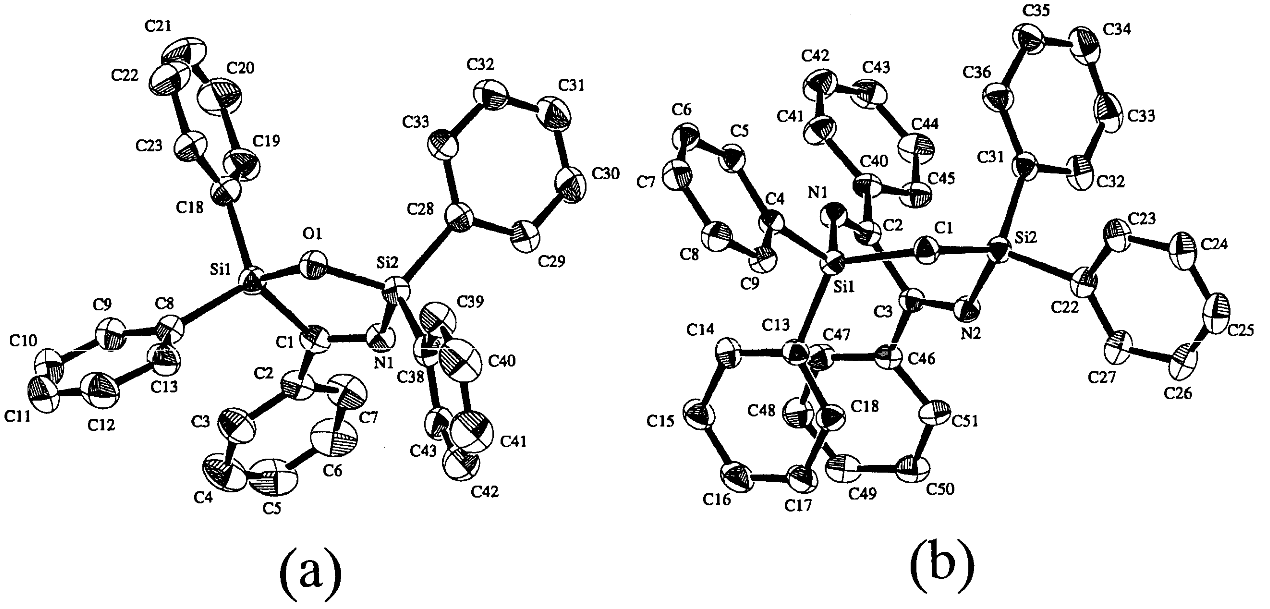


Fig. 1. ORTEP views of (a) **2b** and (b) **3a**, showing only selected non-hydrogen atoms for clarity. Thermal ellipsoids are shown at 30% probability level. Selected bond distances (Å) and bond angles (°) of **2b**: Si(1)–N(1) 1.766(5); Si(1)–C(1) 1.888(6); Si(2)–N(2) 1.755(5); Si(2)–C(1) 1.901(6), 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.

bis-silylation [15] of nitrile, ketone and aldehyde 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.

2. Results and discussion

2.1. Bis-silylation of benzonitrile

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 adduct (**3a**) of **1a** with benzonitrile in good yields (Scheme 1) [14]. The 1:1 adduct (**2b**) of oxadisilirane **1b** with benzonitrile was also obtained under similar reaction conditions.

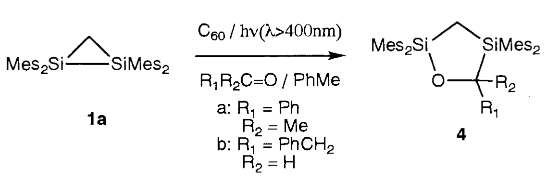
The mass spectrum analyzed by fast atom bombardment mass spectroscopy (FABMS) of the photo-irradiated acetonitrile solution of **1a** in the presence of C_{60} gave the peak corresponding to the 1:1 adduct of **1a** with acetonitrile. Similar results were also obtained by using a catalytic amount of C_{60}, C_{70}, 9,10-dicyanoanthracene, and 2,4,6-triphenylpyrylium tetrafluoroborate. It is noteworthy that C_{60} can act as a photosensitizer.

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 (Fig. 1) [16].

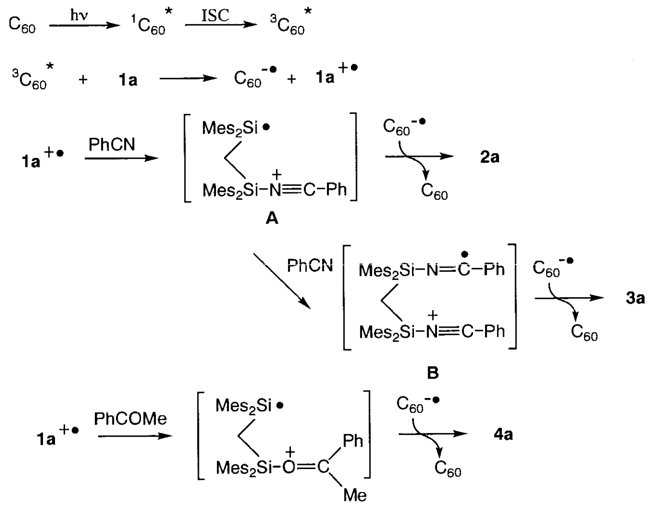
2.2. Bis-silylation of carbonyl compounds

Irradiation of an acetophenone and toluene 1:1 solution of **1a** (2×10^{-3} M) in the presence of catalytic amount of C_{60} with a halogen lamp using a sodium nitrite filter solution (cutoff < 400 nm) resulted in formation of the 1:1 adduct (**4a**) of **1a** with acetophenone in 54% yield (Scheme 2). In the case of phenylacetaldehyde under the same reaction condition, the 1:1 adduct (**4b**) of **1a** with phenylacetaldehyde was also obtained in 30% yield. The structures of **4a** and **4b** were characterized on the basis of spectroscopic data.

We also carried out the photolysis of **1a** with various carbonyl compounds under similar reaction conditions. The bis-silylated products of **1a** with acetone and benzaldehyde were also obtained, but no adduct of **1a** with benzophenone or dipropylketone was detected by means of FABMS spectra. These results reveal that bis-silylation is disturbed due to steric hindrance on a carbonyl moiety.



Scheme 2.



Scheme 3.

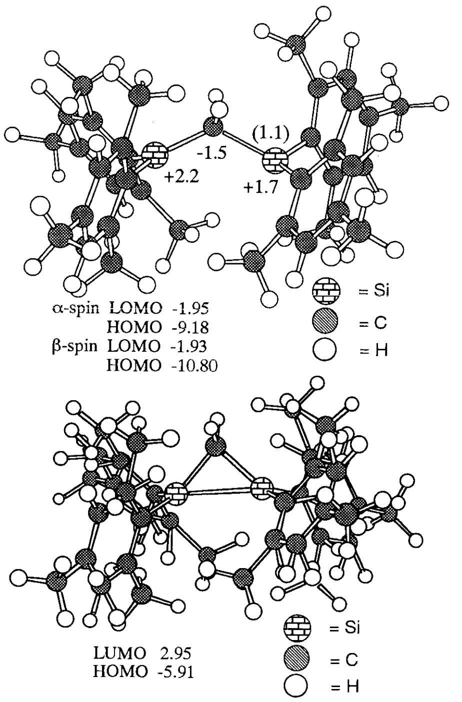


Fig. 2. AM1 optimized structure of $\mathbf{1a}^{+\bullet}$ and **1a**. The charge and spin (in parentheses) densities and HOMO–LUMO levels (eV) at HF/3-21G//AM1 are also shown.

2.3. Mechanism

Disilirane **1** has no absorption 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^{-1} [17,18]. The formation of **2a** and **3a** was suppressed by addition of diazabicyclo[2.2.2]octane or 1,2,4,5-tetramethoxybenzene, each of which has lower oxidation potential than **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. Photochemically generated reactive cation radical $\mathbf{1a}^{+\bullet}$ 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 diradical intermediate via a back electron transfer process (Scheme 3).

The AM1 MO calculations [19] show that $\mathbf{1a}^{+\bullet}$ corresponds to a local minimum on the potential energy surface (Fig. 2). This is also confirmed by non-local hybrid density functional calculations at the B3LYP/6-311G(d,p) level for parent cation radical $\mathbf{1c}^{+\bullet}$ ($R = H$, $X = CH_2$) [19].

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 [5a,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} (Fig. 3a) [9]. 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** (Fig. 3b). 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]. In a solution of **1a** and C_{60} in acetophenone, similar result was also obtained (Fig. 3(c)). 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 the bis-silylated products should be rationalized in terms of the intermediacy of $\mathbf{1}^{+\bullet}$ generated by an electron transfer from **1** to $^3C_{60}^*$.

In order to shed light on the intermediacy of $\mathbf{1}^{+\bullet}$, we carried out the electrochemical generation of $\mathbf{1}^{+\bullet}$. Electrolysis of **1a** (1×10^{-2} M) in benzonitrile using Bu_4NPF_6 as the supporting electrolyte under argon atmosphere resulted in formation of **2a** in 47% yield. By electrolysis of **1b**, **2b** was also obtained under similar reaction condition. These results confirm that the reactive cation radical $\mathbf{1}^{+\bullet}$ can act as an important intermediate in bis-silylation of benzonitrile.

In conclusion, a photoinduced electron transfer bis-silylation is noteworthy because it can proceed under mild condition without a metal catalyst.

3. Experimental

3.1. General procedure

^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra were recorded on a Varian FT-NMR unity plus 500SW or Bruker AVANCE 300 spectrometers. Chemical shifts are referenced to internal tetramethylsilane (δ 0 ppm). IR spectra were measured on a HORIBA FT300 spectrometer. FABMS spectra were obtained with JEOL SX-102. The UV–vis spectra were measured on a Shimadzu UV-2400PC spectrometer. The light source used for a tungsten halogen lamp was a Ushio JCV100V-500W and the irradiation was performed through a sodium nitrite filter solution (cutoff <400 nm). All experiments were carried out under reduced pressure. Benzonitrile and acetophenone were distilled from P_2O_5 in vacuum prior to use. Toluene was distilled from sodium under N_2 atmosphere prior to use. Phenylacetaldehyde was washed by 10% NaOH solution to remove acid and distilled from drierite. Disiliranes were prepared according to the literature method [22].

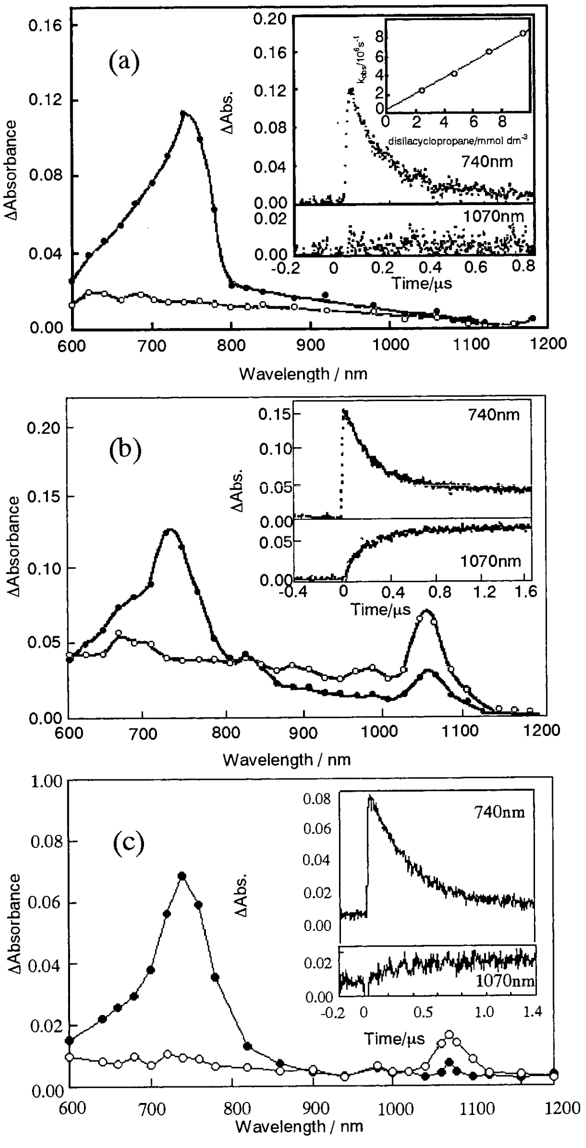


Fig. 3. Transient absorption spectra obtained by 532 nm-laser flash photolysis of C_{60} (0.1 mM) in the presence of disilirane **1a** (2.5 mM) (a) in deaerated benzene. (●) 50 ns and (○) 500 ns. Insert: Time profiles at 740 and 1070 nm and pseudo-first-order plots for the decay of $^{3}C_{60}^{*}$ at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

3.2. Photoreaction of disilirane in the presence of C_{60}

Typically, a 5 ml solution of disilirane **1a** (54.6 mg, 0.1 mmol) in benzonitrile and toluene 1:1 and a 5ml solution of C_{60} (3.6 mg, 5×10^{-3} mmol) in benzonitrile and toluene 1:1 ratio were placed individually in a two legged Pyrex tube. These solutions were mixed after degassed by freeze–pump–thaw cycles under reduced pressure by using a diffusion pump and irradiated with a 500 W halogen lamp (cutoff <400 nm) for 12 h. Separation by preparative HPLC (Japan Analytical Industry LC-08) using toluene as eluent and recrystallization afforded **2a** and **3a** in 51% and 18% yields, respectively. **2a**: waxy solid. ^{1}H-NMR (500 MHz, CD_2Cl_2): δ 7.24 (m, H), 7.15 (brs, 2H), 7.14 (brs, 2H), 6.55 (s, 4H), 6.50 (s, 4H), 2.23 (s, 12H), 2.17 (s, 6H), 2.16 (s, 6H), 2.05 (s, 12H), 1.61 (s, 2H). ^{13}C-NMR (125 MHz, CD_2Cl_2): δ 201.18, 143.60, 143.46, 143.03, 138.45, 137.33, 134.73, 131.51, 129.14*, 128.65, 127.64, 125.89, 24.70, 23.37, 20.31, 20.29, 11.12. *One peak was overlapped by means of gradient HMQC measurement. ^{29}Si-NMR (100 MHz, CD_2Cl_2): δ -0.21, -8.25. FTIR (neat): 1604 cm^{-1}. UV–vis (λ_{max}, hexane): 219, 225, 272 nm. FABMS *m/z* 650 (M + H). **2b**: yellow crystal. m.p. 266°C. ^{1}H-NMR (500 MHz, CD_2Cl_2): δ 7.60 (dd, $J=2.0$, 6.5 Hz, 2H), 7.23–7.38 (m, 7H), 7.00 (d, $J=7.5$ Hz, 4H), 6.99 (d, $J=7.5$ Hz, 4H), 3.07 (q, $J=7.3$ Hz, 4H), 2.68 (q, $J=7.3$ Hz, 4H), 2.62 (q, $J=7.3$ Hz, 4H), 2.43 (q, $J=7.3$ Hz, 4H), 0.77 (t, $J=7.3$ Hz, 12H), 0.61 (t, $J=7.3$ Hz, 12H). ^{13}C-NMR (125 MHz, CD_2Cl_2): δ 201.71, 150.08, 149.13, 145.13, 135.45, 133.08, 129.62, 129.61, 129.03, 127.47, 127.15, 125.93, 125.72, 29.93, 28.32, 15.13, 14.31. ^{29}Si-NMR (100 MHz, CD_2Cl_2): δ -6.38, -19.47. FTIR (neat): 1587 cm^{-1}. UV–vis (λ_{max}, hexane): 213, 239, 253 nm. FABMS *m/z* 708 (M + H). **3a**: Colorless crystal. m.p. 211–212°C. ^{1}H-NMR (500 MHz, CD_2Cl_2): δ 7.69 (d, $J=7.0$ Hz, 4H), 6.86 (s, 4H), 6.84 (d, $J=7.0$ Hz, 2H), 6.76 (t, $J=7.0$ Hz, 4H), 6.21 (s, 4H), 2.96 (s, 12H), 2.53 (s, 12H), 2.75 (s, 6H), 2.13 (s, 6H), 2.12 (s, 2H). ^{13}C-NMR (125 MHz, CD_2Cl_2): δ 178.78, 144.74, 144.26, 139.09, 138.70, 138.64, 135.28, 133.56, 130.88, 130.27, 129.88, 129.04, 127.99, 25.30, 24.72, 21.46, 21.18, 14.94. ^{29}Si-NMR (100 MHz, CD_2Cl_2): δ -15.98.

FTIR (neat): 1604 cm^{-1}. UV–vis (λ_{max}, hexane): 222, 261 nm. FABMS *m*/*z* 753 (M + H). **4a**: Colorless oil. ^{1}H-NMR (300 MHz, CD_2Cl_2): δ 7.08–7.33 (m, 5H), 6.79 (s, 2H), 6.75 (s, 2H), 6.58 (s, 2H), 6.48 (s, 2H), 2.64 (s, 6H), 2.39 (s, 3H), 2.36 (s, 3H), 2.31 (s, 6H), 2.29 (s, 6H), 2.27 (s, 3H), 2.20 (s, 3H), 2.04 (s, 1H), 1.86 (s, 3H), 1.84 (s, 6H), 1.52 (s, 1H). ^{13}C-NMR (75 MHz, CD_2Cl_2): δ 150.4, 143.96, 143.90, 143.44, 142.96, 138.67, 138.38, 138.22, 138.13, 135.52, 134.14, 132.82, 131.69, 129.51, 128.99, 128.68, 128.25, 126.78, 125.22, 124.49, 80.30, 31.80, 25.93, 23.84, 23.23, 22.67, 22.35, 20.46, 20.46, 20.27, 12.09. ^{29}Si-NMR (60 MHz, CD_2Cl_2): δ 4.08, −0.35. FABMS *m*/*z* 667 (M + H). **4b**: Colorless oil. ^{1}H-NMR (300 MHz, CD_2Cl_2): δ 7.25–7.05 (m, 5H), 6.75 (s, 4H), 6.72 (s, 2H), 6.57 (s, 2H), 4.51 (dd, 1H, $J = 2.1$, 11.7 Hz), 2.88 (dd, 1H, $J = 2.4$, 14.7 Hz), 2.66 (dd, 1H, $J = 11.7$, 14.7 Hz), 2.40 (s, 6H), 2.25 (s, 6H), 2.23 (s, 12H), 2.21 (s, 3H), 2.15 (s, 3H), 1.95 (s, 3H), 1.70 (d, 1H, $J = 15.6$ Hz), 1.34 (d, 1H, $J = 15.6$ Hz). ^{13}C-NMR (75 MHz, CD_2Cl_2): δ 144.75, 144.52, 144.22, 143.73, 142.39, 139.25, 139.16, 139.12, 139.07, 135.78, 133.45, 132.46, 131.39, 129.71, 129.48, 129.35*, 129.17, 128.69, 125.84, 72.59, 40.75, 25.43, 24.78, 23.57, 23.49, 23.37, 23.31, 21.30, 21.05, 10.29. *Two peaks overlapped. ^{29}Si-NMR (60 MHz, CD2Cl2): δ 5.34, −4.41. FABMS *m*/*z* 667 (M + H).

3.3. X-ray crystal structure analysis of **2b** and **3a**

The single crystals suitable for X-ray structural determinations were obtained by diffusion of acetonitrile into a solution of **2b** and **3a** in benzene, respectively. Reflection data for both structures were collected using a Rigaku AFC-7R four-circle diffractometer employing graphite monochromated Mo–Kα radiation at 296 K. The data were corrected for Lorentz polarization and crystal absorption. The neutral atom scattering factors used in the refinements were taken from Cromer and Waber [23a] and corrected for anomalous dispersion [23b]. All hydrogen atoms were add in calculated positions (C–H = 0.97 and C–H = 1.08 Å) but not refined. Calculations were performed on an O2 workstation using the TEXSAN crystallographic software package from Molecular Structure Corporation.

3.3.1. Crystallographic data for **2b**

$C_{47}H_{57}NOSi_2$, $M_w = 708.14$, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.618(4)$, $b = 24.758(7)$, $c = 15.958(4)$ Å, $b = 97.39(3)°$, $V = 4160(2)$ Å^3, $D_{calc} = 1.13$ g cm^{-3}, $Z = 4$, $F(000) = 1528.00$, $\mu = 1.20$ cm^{-1}. A colorless crystal of dimensions 0.20 × 0.40 × 0.70 mm was used to collect a total of 11 266 unique reflections in the range $2.8 < 2\theta > 60.0°$. The transmission factors range from 0.60 to 1.00, and the secondary extinction coefficient is equal to 2.929 e^{-8}. The final refinement using 4614 reflections ($I > 3.0\sigma(I)$) and 461 parameters converged $R = 0.063$ and $wR = 0.060$. The corresponding Fourier map show electron density features between 0.34 and −0.32 e Å^{-3}.

3.3.2. Crystallographic data for **3a**

$C_{56.4}H_{61.4}N_2Si_2$, $M_w = 823.49$, monoclinic, space group $P2_1/n$ (no. 14), $a = 12.374(3)$, $b = 25.227(3)$, $c = 15.628(3)$ Å, $b = 98.98(3)°$, $V = 4818(1)$ Å^3, $D_{calc} = 1.13$ g cm^{-3}, $Z = 4$, $F(000) = 1767.2$, $\mu = 1.12$ cm^{-1}. A colorless crystal of dimensions 0.10 × 0.15 × 0.40 mm was used to collect a total of 8518 unique reflections in the range $2.8 < 2\theta > 55.0°$. The data required no decay corrections; the transmission factors range from 0.80 to 1.00, and the secondary extinction coefficient is equal to 2.929 e^{-8}. The crystal lattice contains a benzene molecule whose occupancy parameter refined to 0.9. The final refinement using 4614 reflections ($I > 2.0\sigma(I)$) and 504 parameters converged with $R = 0.069$ and $Rw = 0.076$. The corresponding residual electron density features are between 0.82 and −0.56 e Å^{-3}.

3.4. Laser flash photolysis

Typically, to measurements of transient absorption spectra of $^3C_{60}^*$ and $C_{60}^{-\bullet}$ in the photochemical reaction of disilirane and benzonitrile were performed according to the following procedures. A deaerated benzonitrile solution containing C_{60} (1×10^{-4} M) and disilirane (5×10^{-3} M) was excited by a Nd: YAG laser (Quanta-Ray, GCR-130, 6 ns FWHM) at 532 nm with the power of 7 mJ. A pulsed xenon flash lamp (Tokyo Instruments, XF80-60, 15 J, 60 ms FWHM) was used for the probe beam, which was detected with a Ge-APD module (Hamamatsu, C5331-SPL) after passing through the photochemical quartz vessel (10 × 10 mm^2) and a monochromator. The output from Ge-APD module was recorded with a digitizing oscilloscope (HP54510B, 300 MHz).

3.5. Electrochemistry

Controlled-potential bulk electrolysis was carried out using a BAS CV-50W voltammetry analyzer. A conventional three-electrode cell was used for controlled-potential bulk electrolysis and consisted of a platinum working electrode, a platinum counter electrode, and a saturated calomel reference electrode (SCE). In a cyclic voltammogram of disilirane (**1a**) measured in benzonitrile-BuN_4PF_6 solution, an irreversible oxidation peak was observed at 0.71 V (versus SCE). The electrolysis of **1a** (1×10^{-2} M) was conducted at controlled potential of 0.91 V (vs. SCE) in benzonitrile using Bu_4NPF_6 as the supporting electrolyte under argon atmosphere. After electrolysis, Bu_4NPF_6 and benzonitrile were removed. Product (**2a**) was obtained in 47% yield and identified by FABMS and NMR spectroscopic analyses.

4. Supplementary material

Crystallographic data for the structural analysis (atomic coordinates, bond lengths and angles, and thermal parameters) has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 102853 for **2b** and 102854 for **3a**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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