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Charge-transfer Complex Formation and Photo-induced Electron-transfer Reaction of Dibenzo-7-silabicyclo[2.2.1]hepta-2,5-dienes

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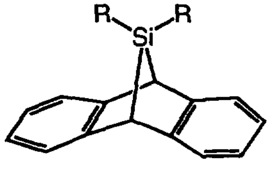
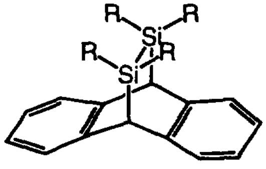
Abstract: Dibenzo-7-silabicyclo[2.2.1]hepta-2,5-dienes (**1a**, **1b**) are excellent electron donors because of effective σ-π conjugation between the orbitals of C-C π bonds and Si-C σ bonds. Some of their donor properties are demonstrated by the reactions with some electron acceptors. When **1a** and **1b** are mixed with tetracyanoethylene, facile formation of charge-transfer complexes was observed. In the 2,4,6-triphenylpyrylium tetrafluoroborate-sensitized photoreaction of **1b**, the corresponding difluorosilane and anthracene were obtained in good yields. The structural and electronic features of radical cation $\mathbf{1a}^{+\bullet}$ were provided by semiemperical molecular orbital calculation. In addition, the structure of **1a** in crystals was determined by X-ray crystallography and compared with that obtained by the calculation.

INTRODUCTION

Electron-transfer chemistry of group 14 organometallic compounds has been producing fascinating results.[1-6] β-silylated olefinic and aromatic compounds are the most commonly used electron-donors since the HOMOs of these substrates are significantly destabilized due to σ-π conjugation between the orbitals of C-C π bonds and Si-C σ bonds.[7] Recently, we indicated that dibenzo-7-silabicyclo[2.2.1]hepta-2,5-dienes (**1**) and 7,8-disilabicyclo[2.2.2]octa-2,5-dienes (**2**) act as electron donors to undergo skeletal rearrangement and C-Si bond cleavage, respectively.[8] Matsumoto and coworkers have also reported electron donating properties of some polycyclic carbosilanes by investigating charge-transfer (CT) complex formation.[9] As a part of our continuing studies of electron-transfer reaction of organosilicon compounds, we now report donor-acceptor interaction of **1** with some electron acceptors. Also described are structural and electronic properties of both the ground state neutral **1** and the corresponding radical cation $\mathbf{1}^{+\bullet}$ on the basis of semiemperical molecular orbital calculation.



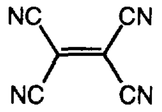
1a: R = 2,6-dimethylphenyl, **1b**: R = mesityl



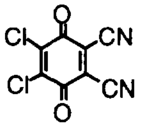
2a: R = Me, **2b**: R = ^{i}Pr, **2c**: R = CH$_2$^{t}Bu

RESULTS AND DISCUSSION

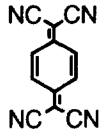
Formation of CT Complexes between 1 and Electron Acceptors. Since **1a** and **1b**[10] have fairly low oxidation potentials (**1a**: E_{ox} = +1.45 V vs SCE, **1b**: E_{ox} = +1.40 V vs SCE), we investigated CT complex formation with electron acceptors. Upon mixing **1a** and tetracyanoethylene (TCNE) in CH_2Cl_2, an intense coloration with an absorption maximum at 467 nm developed immediately. According to Mulliken's charge-transfer theory,[11] the absorption bands of the CT complex shift to a longer wavelength region as the magnitude of electron donating abilities of donors increases. Thus, when **1b**, which has a lower oxidation potential than **1a**, was used as the electron donor, a substantial red shift was observed affording an absorption maximum at 507 nm. Previously, we[8a] and Matsumoto's group[9c] have reported that **2a-c** and TCNE form CT complexes with absorption maxima at 630~650 nm, and the donor properties of **2a-c** are attributable to the effective overlapping of π-orbitals of the aromatic ring with the benzylic Si-C σ bonds. Meanwhile, in the case of **1**, such σ-π conjugation should operate less effectively than does in **2** as expected from that dihedral angle between the π-orbitals of the anthracene moiety and the benzylic Si-C σ bonds is 43° (calculated by the MOPAC PM3 method, see below), much larger than that of **2c** (17°).[9c] Similarly, **1b** and benzoquinone derivatives, chloranil (CL), tetracyanoquinodimethane (TCNQ), and dichlorodicyanobenzoquinone (DDQ) afforded CT complexes with absorption maxima as summarized in Table 1, whereas those of **1a** could not be observed even with DDQ probably due to spectral overlapping by intense absorption of the acceptors. There seems to be a linear correlation between the charge transition energies ($h\nu_{CT}$) and the reduction potentials (E_{red}) of acceptors for the **1b**-quinone system as expected from Mulliken's charge-transfer theory.[1f,g,11]



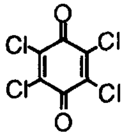
TCNE



DDQ



TCNQ



CL

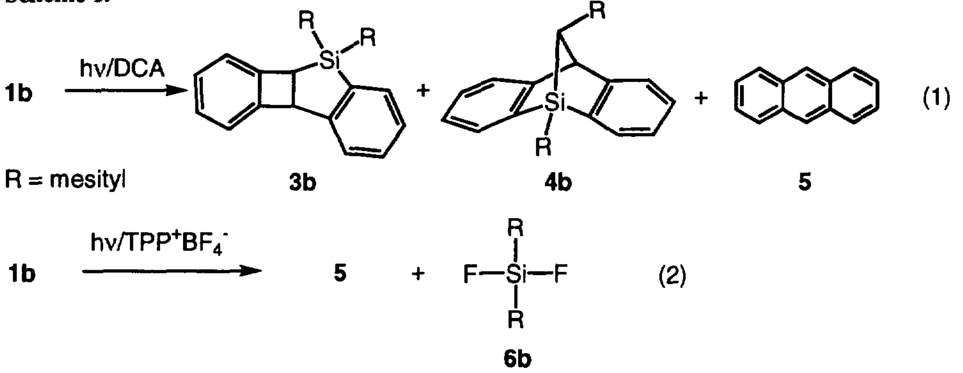
Table 1. UV Absorption Maxima of CT Complexes of 1b with Acceptors.

Acceptor	E_{red} [V] vs SCE[12]	λ_{CT} [nm]	$h\nu_{CT}$ [eV]
TCNE	+0.24	507	2.45
DDQ	+ 0.52	500	2.48
TCNQ	+ 0.18	445	2.79
CL	+ 0.04	420	2.95

Photosensitized Reaction of 1 with a Pyrylium Salt. Recently we reported that **1b** underwent skeletal rearrangement under photolytic conditions using 9, 10-dicyanoanthracene (DCA) as a sensitizer (Scheme 1, eq.

1).[8b] It is of particular interest to examine whether such a rearrangement takes place under other electron-transfer conditions. Since pyrylium salts have been used in various photo-induced electron-transfer reactions,[13] we studied the photoreaction of **1b** in the presence of 2,4,6-triphenylpyrylium tetrafluoroborate ($TPP^+BF_4^-$). When a CH_2Cl_2 solution of **1b** (2.8×10^{-2} M) in the presence of $TPP^+BF_4^-$ (1.5×10^{-2} M) was irradiated with 500 W tungsten-halogen lamps (passing through an aqueous $NaNO_2$ solution filter, cutoff < 400 nm), **1b** was rapidly consumed and anthracene (**5**) and difluorodimesitylsilane (**6b**)[14] were obtained in 89 and 59 %, respectively, as shown in Table 2 (Scheme 1, eq. 2). The following observation is supportive of an electron-transfer mechanism. (i) The fluorescence of $TPP^+BF_4^-$ was efficiently quenched with **1b** ($k_q \tau = 70$ M^{-1}). (ii) The free energy change (ΔG)[15] of electron-transfer process between **1b** and $TPP^+BF_4^-$ is calculated to be -29.9 kcal/mol, which is indicative of exothermic electron-transfer from **1b** to the excited singlet state of $TPP^+BF_4^-$. The reaction did not occur without the sensitizer or under a dark condition and was suppressed by addition of electron donors such as 1,4-diazabicyclo[2.2.2]octane ($E_{ox} = + 0.70$ V vs SCE). On the other hand, neither exciplex emission nor charge-transfer absorption was observed between **1b** and the acceptors ($TPP^+BF_4^-$ and DCA). Whereas the results presented above cannot exclude possibilities of initial formation of an exciplex or a charge-transfer complex, it would be reasonable to discuss these reactions as a process induced by initial electron-transfer from **1b** to the acceptors.

Scheme 1.

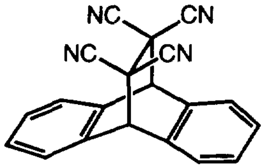


A proposed reaction mechanism for **1b** is shown in Scheme 2. Initially, the bridge Si-C bond would be oxidized and cleaved by a nucleophilic attack of BF_4^- to form an open intermediate **A**, which may subsequently release neutral anthracene and fluorosilyl radical **B**. Since it has been reported that silyl radicals have quite low ionization potentials,[16] **B** might undergo further one-electron oxidation to give a silyl cation **C**, which should react with BF_4^- as a F^- source to afford difluorosilane **6b**. Recent reports have demonstrated that nucleophilies such as alcohols have an important role in the cleavage reactions of Si-Si and Si-C bonds of organosilicon radical cations.[1] Furthermore, the electrochemical oxidation of cyclic polysilanes $(R_2Si)_n$ using $n\text{-}Bu_4N^+BF_4^-$ as supporting electrolyte has been reported to give α,ω-difluoropolysilanes $F\text{-}(R_2Si)_n\text{-}F$, and explained in terms of fluorinative Si-Si bonds cleavage of polysilane radical cations.[17] These reports would offer a basis for our mechanistic account.

In the $TPP^+BF_4^-$-sensitized reaction of **1b**, neither **3b** nor **4b** was detected in contrast to the case of the DCA-sensitization,[8b] which suggests that the fluorinative cleavage reaction should occur at an earlier stage than the rearrangement in the total reaction pathway. The Si-F bonds have so large bond formation energies[18] that fluoride ions might be transferred quite rapidly from BF_4^- to radical cation **1b**$^{+\bullet}$ and eventually furnish **6b**. In fact, **6b** was readily produced when DCA-sensitized photoreaction of **1b** was carried out in the presence of $n\text{-}Bu_4N^+BF_4^-$ whereas production of the rearrangement products, **3b** and **4b**, was suppressed. Under the same conditions, **3b** was confirmed to be stable and **4b** was found to be photoreactive, but afforded neither **5** nor **6b** at all. Since TCNE is also known as a strong acceptor to oxidize various donors[19] we performed photolysis of a CH_2Cl_2 solution of **1b** and TCNE in the presence of $n\text{-}Bu_4N^+BF_4^-$ with visible light. As expected, **1b** was facilely consumed to give **6b** along with the Diels-Alder adduct of anthracene and TCNE (**7**)[20] as shown in Table 2.

Table 2. Photosensitized Fluorination

Substrate	Reaction Condition	Time/h	Coversion/%	Products and Yields/%				
				3b	4b	5	6b	7
1b	hν / $TPP^+BF_4^-$ / CH_2Cl_2	2	100	0	0	89	59	
1b	hν / DCA / $n\text{-}Bu_4N^+BF_4^-$ /CH_2Cl_2	3	78	18	18	36	14	
1b	hν / DCA /CH_2Cl_2	3	89	31	36	18	0	
1b	hν / TCNE / $n\text{-}Bu_4N^+BF_4^-$ /CH_2Cl_2	3	85	18	18	0	14	36



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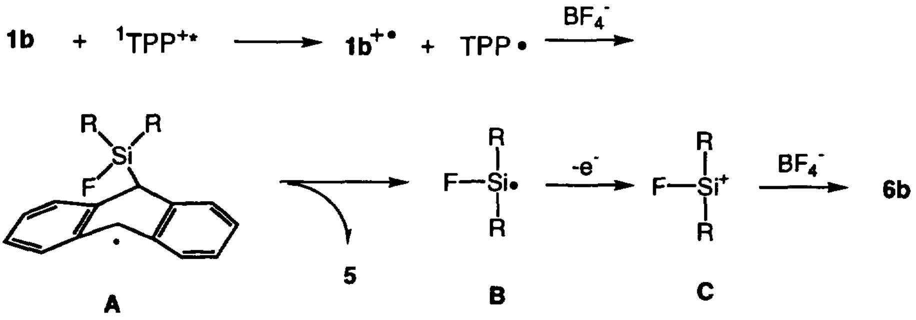
Scheme 2.



Structure Determination and Semiemperical MO Calculation. The optimized structure of **1a** and the corresponding radical cation **1a**$^{+\bullet}$ are calculated by the MOPAC PM3[21] method, which are shown in Figure 1 with selected geometrical parameters in Table 3. To verify the validity of the calculation, we carried out the

X-ray analysis of **1a** in crystals. Two sets of four molecules of **1a** (**1a**-A and **1a**-B) are contained in the unit cell and the molecular structure of **1a**-A is shown with important bond lengths and angles in Figure 2 and Table 3. The bond lengths and angles are fairly close to with those reported for related silanorbornadiene derivatives.[22] The bridge Si-C bonds are slightly longer than normal Si-C bonds.[23] Similar bond elongation in silanorbornadiene skeleton was reported and explained in terms of delocalization of electron density of the bridge Si-C σ bond to the π bonds of the anthracene moiety.[22c] Validity of the optimized structure of **1a** was thus supported by a comparison with that obtained by the X-ray analysis. Adiabatic ionization potentials (IP) of **1a** and **1b** were also estimated to be 7.42 and 7.36 eV, respectively, by calculating the gap of heats of formation between the neutral and the radical cation. As shown in Table 4, these values are reasonable since the calculated IP values for bis- and tetrakis-Me_3SiCH_2 benzenes as related compounds show good consistency with those measured by photoelectron spectroscopy.[24] The calculated HOMO drawing of **1a** is illustrated in Figure 3. As reported by Bock and Alt,[7a] the HOMO is surely delocalized on both the aromatic π systems and the benzylic C-Si bond.

We investigated the characteristics of the radical cation **1a**$^{+\bullet}$ to gain insight into the reaction mechanism. The most important structural features of the **1a**$^{+\bullet}$ are as follows, (i) the one of the bridge Si-C bond (Si(1)-C(1), 2.60Å) being much longer compared to the other (Si(1)-C(4), 1.98Å) and to those of neutral **1a** (Si(1)-C(1), 2.02Å; Si(1)-C(4), 2.03Å), (ii) the marked flattening of both the Si(1) atom and the C(1) atom (sum of

Table 3. Selected Bond Distances (Å) and Angles (°)

	X-ray Data		Calculated Data	
	1a-A	**1a**-B	**1a**	**1a**$^{+\bullet}$
Si(1)-C(1)	1.944(5)	1.939(5)	2.024	2.599
Si(1)-C(4)	1.930(5)	1.956(5)	2.026	1.983
Si(1)-C(7)	1.905(5)	1.904(5)	1.875	1.821
Si(1)-C(8)	1.886(5)	1.914(5)	1.878	1.835
C(1)-C(6)	1.509(7)	1.533(7)	1.491	1.434
C(1)-C(2)	1.527(7)	1.504(7)	1.491	1.433
C(4)-C(5)	1.527(7)	1.506(7)	1.488	1.480
C(4)-C(3)	1.554(8)	1.508(7)	1.493	1.479
C(6)-C(5)	1.413(7)	1.397(7)	1.417	1.426
C(2)-C(3)	1.375(8)	1.417(7)	1.417	1.427
C(1)-Si(1)-C(4)	80.4(2)	79.5(2)	78.379	70.752
C(1)-Si(1)-C(7)	112.3(2)	112.3(2)	111.543	104.552
C(1)-Si(1)-C(8)	117.9(2)	118.9(2)	119.713	114.344
C(4)-Si(1)-C(7)	119.2(2)	119.4(2)	117.881	123.273
C(4)-Si(1)-C(8)	110.5(2)	110.3(2)	114.132	114.917
C(7)-Si(1)-C(8)	113.0(2)	112.9(2)	111.715	117.580
Si(1)-C(1)-C(6)	97.8(3)	97.6(3)	96.418	82.076
Si(1)-C(1)-C(2)	97.0(3)	98.1(3)	95.637	83.154
C(6)-C(1)-C(2)	107.4(4)	107.1(4)	107.362	117.662
Si(1)-C(4)-C(5)	96.4(3)	96.2(3)	96.485	97.047
Si(1)-C(4)-C(3)	97.1(3)	98.8(3)	96.233	99.124
C(5)-C(4)-C(3)	107.6(4)	107.7(4)	107.663	111.146
C(1)-C(6)-C(5)	111.6(4)	109.8(4)	112.721	117.444
C(4)-C(5)-C(6)	110.3(4)	112.3(4)	112.208	114.007
C(1)-C(2)-C(3)	111.2(5)	111.5(4)	112.547	117.383
C(4)-C(3)-C(2)	111.7(5)	110.2(4)	112.363	113.932

angles, C(7)-Si(1)-C(8), C(7)-Si(1)-C(4), and C(4)-Si(1)-C(8) being 355.8°; sum of angles, C(2)-C(1)-C(6), C(2)-C(1)-H(1), and C(6)-C(1)-H(1) being 356.4°), (iii) the slight but appreciable shortening of Si(1)-C(4), Si(1)-C(7), Si(1)-C(8), C(1)-C(2), and C(1)-C(6) bonds on the transition from **1a** to **1a**$^{+\bullet}$. Some electronic properties of the optimized radical cation are summarized in Table 5. A significant population of the positive charge is observed at the Si(1) atom whereas the spin population is more predominant at the anthracene unit than at the silicon atom and the 2,6-dimethylphenyl group. Therefore, it is suggested that Si(1)-C(1) bond of **1a**$^{+\bullet}$ has a tendency to dissociate to a cationic silyl site and a diarylmethyl radical site. Similar structural and electronic aspects were reported for radical cation [t-Bu$_3$SiH]$^{+\bullet}$ calculated by the MOPAC AM1 method.[25]

In addition to the HOMO of **1a**, these findings described above indicate that one electron is removed from one of the bridge Si-C bonds, which would be weakened subsequently to afford the relaxed form of **1a**$^{+\bullet}$ as depicted in Figure 1. The presence of nucleophiles such as alcohol and fluoride ion should accelerate the cleavage of the Si-C bond.

Figure 1. Optimized Structures of the Neutral 1a (left) and the Radical Cation of 1a (right).

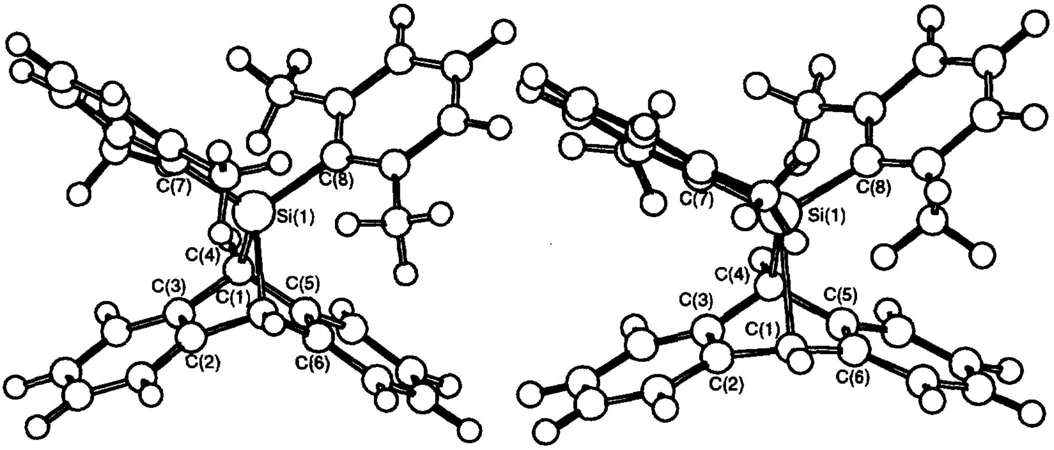


Figure 2. ORTEP Drawing of 1a.

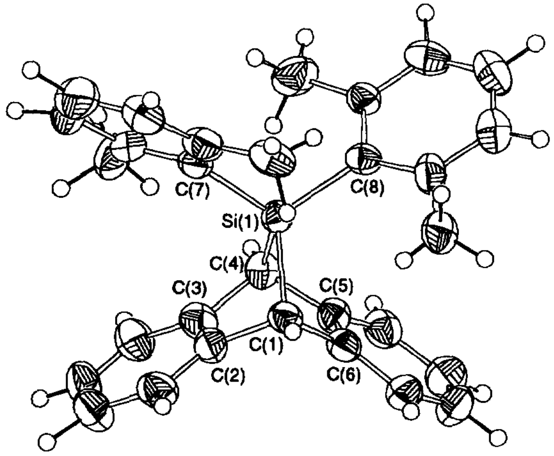


Figure 3. Calculated HOMO Orbital for 1a.

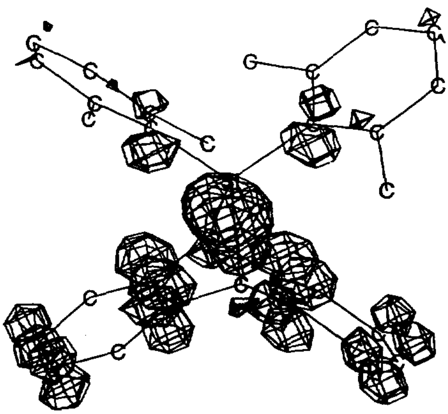


Table 4. Ionization Potentials (IP) of 1a-b and Some Benzylic Silanes

Silane	IP /eV*
$Me_3SiCH_2C_6H_5$	8.06 (8.35)
1,2-$(Me_3SiCH_2)_2C_6H_4$	7.71 (8.05)
1,4-$(Me_3SiCH_2)_2C_6H_4$	7.63 (7.75)
1,2,4,5-$(Me_3SiCH_2)_4C_6H_2$	7.01 (7.10)
1a	7.42
1b	7.36

*Experimental values are in parentheses.(see text)

Table 5. Charge and Spin Density of Radical Cation 1a$^{+\cdot}$

Atom	Charge (ΔCharge*)	Spin Density
Si(1)	+0.905 (+0.443)	+0.200
C(1)	-0.072 (-0.006)	-0.154
C(2)	-0.061 (-0.001)	+0.467
C(3)	-0.073 (-0.018)	-0.417
C(4)	-0.058 (+0.029)	+0.633
C(5)	-0.069 (-0.018)	-0.425
C(6)	-0.061 (+0.001)	+0.499
C(7)	-0.257 (-0.063)	-0.155
C(8)	-0.264 (-0.067)	-0.111

Fragment	Charge(ΔCharge*)	Spin Density
Si atom	+0.904 (+0.443)	+0.200
2,6-dimethylphenyl	-0.134 (+0.178)	+0.022
anthracene	+0.229 (+0.379)	+0.778

*Change of the charge from the neutral to the cation radical.

EXPERIMENTAL

NMR spectra were recorded with a Varian Unity-plus 500 spectrometer. Deuteriated chloroform and benzene were used as the solvent. Mass spectral data were obtained on a Shimadzu QP-1000 mass spectrometer. UV-visible spectra were obtained with a HITACHI U-3300 spectrometer. GLC-analyses were carried out on a Shimadzu GC-14A equipped with a 0.25 mm x 25 m CBP1 capillary column. Cyclic voltammograms of **1** were obtained on 0.1 M n-Bu_4NClO_4/CH_2Cl_2 solution (vs SCE; scan rate, 200 mV/s; Hokuto Denko Ltd., a potentiostat/galvanostat HA-501 and a function generator HB-104). Oxidation potentials (E_{ox}) of **1a** and **1b** are + 1.40 and +1.45 eV vs SCE (irreversible), respectively. The ΔG values were calculated according to the Rehm-Weller equation (ΔG(kcal/mol)=23.06[$E(D/D^+)-E(A^-/A)-e_o^2/\varepsilon a-\Delta E_{0.0}$])$^{9)}$ by using the excited singlet energies of $TPP^+BF_4^-$ (2.83 V), the reduction potentials of $TPP^+BF_4^-$ (-0.29 V vs SCE),$^{13)}$ and -0.12 eV for $e_o^2/\varepsilon a$ in CH_2Cl_2.$^{26)}$ Quenching of $TPP^+BF_4^-$ fluorescence was measured by using a HITACHI F-4500 fluorescence spectrometer. Irradiation was carried out by two 500-W tungsten-halogen lamps using a Pyrex filter in a water bath while N_2 passed through the photolysate. DCA, CL, DDQ, TCNQ, n-$Bu_4N^+BF_4^-$ (Tokyo Kasei) and $TPP^+BF_4^-$ (Aldrich) were used as received. TCNE (Tokyo Kasei) was used after sublimation *in vacuo*. Compounds **1a**$^{10)}$, **1b**$^{10)}$, **6b**$^{14)}$, and **7**$^{20)}$ were prepared according to the literature.

*$TPP^+BF_4^-$-sensitized Photoreactions of **1b**.* In a typical experiment, **1b** (2.8×10^{-2} M) was dissolved in a CH_2Cl_2 solution (4 ml) with $TPP^+BF_4^-$ (1.5×10^{-2} M) as a sensitizer, and this solution was photolyzed. The reaction was monitored by GLC. Formation of **5** and **6b** was confirmed by comparison of their retention time on GLC with those of the authentic sample and GC-MS analysis. The yields of **5** and **6b** were determined by ^{1}H-NMR analysis.

*DCA-sensitized Photoreactions of **1b**.* In a typical experiment, a CH_2Cl_2 solution (4 ml) of **1b** (1.7×10^{-2} M) and DCA (1.3×10^{-3} M) in the presence of $n\text{-}Bu_4N^+BF_4^-$ (1.7×10^{-1} M) was photolyzed and the reaction was monitored by GLC. Formation of **5** and **6b** was confirmed by comparison of its retention time on GLC. The yields of **3b, 4b, 5**, and **6b** were determined by ^{1}H-NMR analysis. **2**: colorless crystals; mp 177~179°C; ^{1}H-NMR($CDCl_3$) δ 7.63(d, 1H, J=7.3Hz), 7.48(d, J=7.3Hz, 1H), 7.32(t, J=7.3Hz, 1H), 7.13(t, 1H, J=7.3Hz), 6.93~6.90(m, 2H), 6.745(1H, t, J=7.3Hz), 6.744(s, 2H), 6.67(s, 2H), 5.89(d, 1H, J=7.3Hz), 5.21(d, 1H, J=4.6Hz), 4.32(d, 1H, J=4.6Hz), 2.25(s, 9H), 2.21(s, 3H), 1.94(brs, 6H); ^{13}C-NMR($CDCl_3$) δ 150.90(s), 149.97(s), 145.62(s), 143.07(s), 142.92(s), 139.84(s), 138.55(s), 138.33(s), 134.97(d), 133.62(s), 133.26(s), 129.67(d), 129.12(d), 128.32(d), 126.86(d), 126.69(d), 125.47(d), 125.39(d), 123.34(d), 120.37(d), 55.10(d), 39.30(d), 24.86(q), 24.49(q), 21.11(q), 20.96(q); ^{29}Si-NMR($CDCl_3$) δ -7.32; MS m/z (%) 444(M, 19), 429(100), 368 (23); Anal. Calcd for $C_{32}H_{32}Si$: C, 86.43; H, 7.25. Found: C, 86.54; H, 7.27. **3**: colorless crystals; mp 226~227°C; ^{1}H-NMR($CDCl_3$) δ 7.70(d, 1H, J=7.3Hz), 7.52(d, 1H, J=7.3Hz), 7.36(d, 1H, J=7.3Hz), 7.13~7.05(m, 2H), 7.02~6.93(m, 5H), 6.70(s, 2H), 4.47 (d, 1H, J=1.4Hz), 3.64(d, 1H, J=1.4Hz), 2.51(s, 6H), 2.31(s, 3H), 2.13(s, 3H), 2.07(brs, 6H); ^{13}C-NMR($CDCl_3$) δ 156.37(s),153.23(s), 145.52(s), 143.03(s), 141.97(s), 140.77(s), 137.70(s), 136.07(s), 134.72(s), 132.14(d), 132.11(d), 129.69(d), 128.67(d), 128.04(d), 127.69(d), 125.71(d), 125.34(s), 125.03(d), 124.81(d), 122.34(d), 67.18(s), 59.05(s), 23.27(q), 22.77(q), 21.23(q), 20.57(q); ^{29}Si-NMR($CDCl_3$) δ -9.70; MS m/z (%) 444(M^+, 15), 429(100); Anal. Calcd for $C_{32}H_{32}Si$: C, 86.43; H, 7.25. Found: C, 86.22; H, 7.40.

*Photolysis of the **1b**-TCNE CT complex.* A CH_2Cl_2 solution (4 ml) containing **1b** (4.5×10^{-2} M), TCNE (1.7×10^{-1} M), and $n\text{-}Bu_4N^+BF_4^-$ (9.0×10^{-2} M) was photolyzed and the reaction was monitored by TLC. Formation of **6b** and **7** was confirmed by comparison of ^{1}H-NMR spectra with those of the authentic samples. The yields of **6b** and **7** were also determined by ^{1}H-NMR analysis.

X-ray Crystal Analysis. Intensity data were collected with Mo Kα radiation (graphite monochrometer λ=0.71073Å) on a Rigaku AFC-4 diffractometer. Crystal data for **1a**,: $C_{30}H_{28}Si$ (fw 416.64), orthorhombic $Pna2_1$; a= 16.681(2) Å; b = 8.701(2) Å; c= 31.817(7) Å; V=4618(2) Å^3; Z=8. A total of 5725 reflections within 2θ = 55° were measured by the ω scan method with a scan rate of 4°/min. The final R factor was 0.056 (Rw= 0.072) for 3943 reflections of Fo> 3σ (Fo).

Semiempericał Calculation. The calculations were carried out by the CAChe MOPAC program (Release 3.8, available from SONY Tektronix Co. Ltd.) on an Apple Macintosh computer. Optimized structures of the neutrals and the radical cations were obtained by using restricted and unrestricted Hartree-Fock wave function, respectively.

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