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Formation and X-Ray Crystal Structure of Charge-Transfer Complexes of Silacyclopentadiene Derivatives with Quinones

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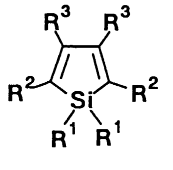
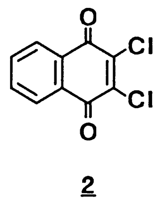
Silacyclopentadiene derivatives form charge-transfer complexes with various quinones which have been characterized by spectroscopic data and X-ray crystallographic determination.

The chemistry of charge-transfer complexes including organosilicon compounds such as peralkylpolysilanes,1) benzylsilanes,2,3) and benzyldisilanes4) has been investigated extensively in the last two decades. These organosilicon compounds have relatively low ionization potentials due to σ-5) and σ-π3) conjugation and act as efficient electron donors. Recent studies on silacyclopentadiene derivatives (siloles) indicate that they have fairly low ionization6) and oxidation7) potentials and donate an electron to an acceptor in photo-induced electron transfer reactions.7) In this paper, we report the formation of charge-transfer complexes of silacyclopentadiene derivatives with various quinones and describe spectroscopic and X-ray crystallographic properties of the system.

A yellow solution of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene **1a** in dichloromethane turned the color when a small amount of quinones **2-8** was added to it. In UV-visible absorption spectra, new and broad bands appeared in the longer wavelength region than those due to **1a** and the quinones (Fig. 1). The maximum wavelengths and the colors are 478 nm, orange (**2**); 525 nm, red (**3**); 526 nm, red (**4**); 567 nm, violet (**5**); 600 nm, green-blue (**6**); 607 nm, blue-green (**7**); 860 nm, green (**8**), respectively. The maximum wavelengths are highly dependent on the electron-accepting property of the quinones, and tend to shift to the longer wavelength region as the electron-accepting property of the



1a : R^1=Me, R^2=Ph, R^3=H
1b : R^1=Me, R^2=R^3=Ph
1c : R^1=R^2=R^3=Ph
1d : R^1=R^3=Me, R^2=H



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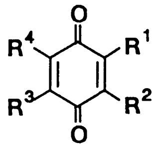

3 : R^1=R^3=Cl, R^2=R^4=H
4 : R^1=R^4=Cl, R^2=R^3=H
5 : R^1=R^2=R^3=R^4=F
6 : R^1=R^2=R^3=R^4=Cl
7 : R^1=R^2=R^3=R^4=Br
8 : R^1=R^2=Cl, R^3=R^4=CN

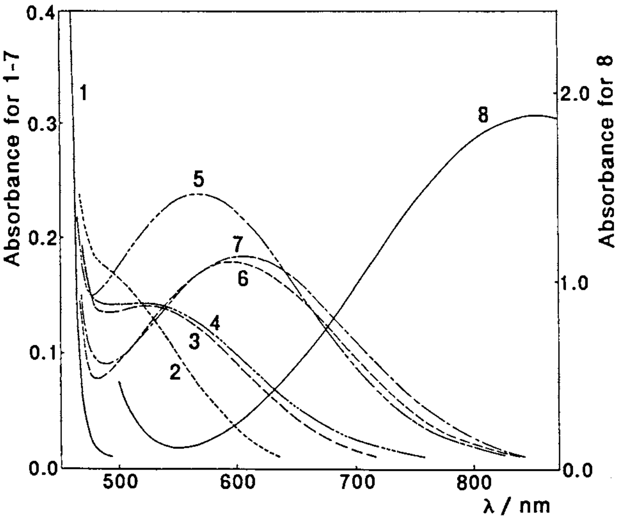

Fig. 1. Charge-transfer absorption spectra of **1a**-quinone complexes in dichloromethane. The concentration of **1a** is 0.19 M in every case. The concentrations of quinones are as follows. 1: none; 2: **2**, 3.7×10^{-3} M; 3: **3**, 3.1×10^{-3} M; 4: **4**, 3.2×10^{-3} M; 5: **5**, 2.5×10^{-3} M; 6: **6**, 1.8×10^{-3} M; 7: **7**, 2.1×10^{-3} M; 8: **8**, 3.1×10^{-3} M (1 M = 1 mol dm^{-3}).

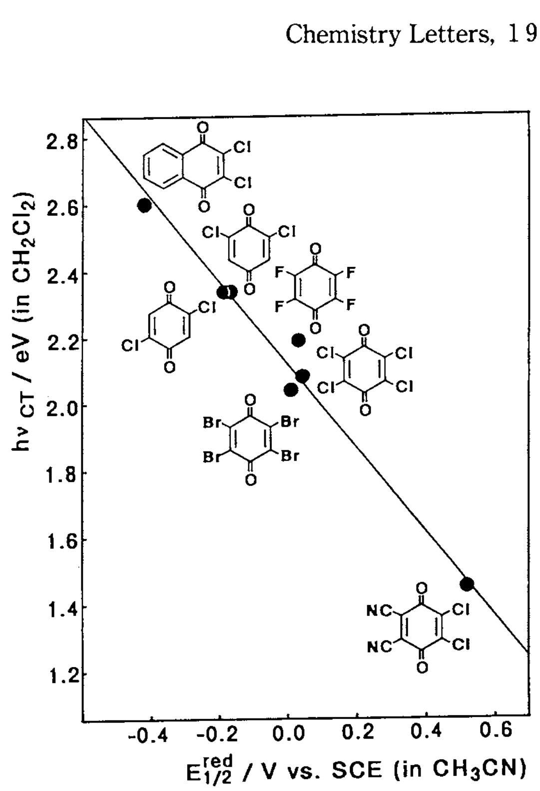

Fig. 2. The plot of charge-transfer transition energies of **1a**-quinone complexes against half-wave reduction potentials of the quinones.

quinones increases. In the case of an extremely strong acceptor **8**, the absorption band extends to the infrared region. The correlation between charge-transfer transition energies ($h\nu_{CT}$) for the **1a**-quinone complexes and half-wave reduction potentials of the quinones ($E^{red}_{1/2}$ vs. SCE) is shown in Fig. 2. A good linear relationship was obtained, expressed as

$$h\nu_{CT} = -1.24 E^{red}_{1/2} + 2.12 \qquad (1)$$

with a correlation coefficient of -0.987. The expression is in good accord with Mulliken's charge-transfer theory,[8] expressed as

$$h\nu_{CT} = \mathrm{IP(Donor)} - E_A\mathrm{(Acceptor)} - \omega \qquad (2)$$

because $E^{red}_{1/2}$ and E_A are measures of the electron-accepting ability in solutions and in the gas phase, respectively. These features indicate that the new absorption bands are attributed to the charge-transfer interaction between **1a** and quinones.

Other silacyclopentadiene derivatives (1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene **1b** and 1,1,2,3,4,5-hexaphenyl-1-silacyclopentadiene **1c**) also formed charge-transfer complexes with the quinones, but their absorption bands are extremely weak. For example, λ_{max} and absorbance of the charge-transfer absorption of (**1a-c**)-DDQ(**8**) complexes (**1a-c**: 0.11 mol dm^{-3}, **8**: 0.005 mol dm^{-3}) in dichloromethane are as follows; **1a-8**: 860 nm (A_{max} 2.1), **1b-8**: 800 nm (A_{max} 0.08), and **1c-8**: 740 nm (A_{max} 0.04). The order of maximum wavelengths agrees with that of oxidation potentials of **1a** (1.24 V), **1b** (1.31 V), and **1c** (1.43 V).[9] The intensity of the charge-transfer absorption (**1a**>>**1b**>**1c**) seems to reflect the degree of planarity of silacyclopentadiene derivatives since CT formation should be preferable between planar chromophores. Indeed, X-ray crystallographic structure of **1a** has been reported to be almost planar (the dihedral angle between the silacyclopentadiene ring and the benzene ring is 14°),10) while benzene rings of **1b** cannot exist in the same plane of the silacyclopentadiene ring (the dihedral angles are 30-70°).11)

Although isolation of the charge-transfer complexes of organosilicon compounds were rather difficult,1-4) we succeeded in obtaining a complex of **1a** with fluoranil 5 as crystals. A solution of **1a** and 5 (1 : 2) in dichloromethane was evaporated by a rotary evaporator to afford immediately violet prisms of the complex quantitatively. The crystals are stable, but on gentle heating for a few minutes or on standing for several days, fluoranil sublimes and only **1a** remains. A single crystal of the complex was sealed in a glass capillary and subjected to X-ray intensity measurement. Figure 3 shows the crystal structure of the complex.12) The complex consists of **1a** and 5 in the ratio of 1 : 2. The silole molecule has an exact 2-fold symmetry. Two molecules of the quinone are located over both the benzene rings of the silole. The interplanar distances are 3.51 and 3.49 Å, respectively. The silacyclopentadiene ring is almost planar and the dihedral angle between the silacyclopentadiene ring and the benzene ring is 7.5°. Therefore, the structure of **1a** in the complex is more planar than in **1a**.10) It is noted that the position of 5 is not over the silacyclopentadiene ring but over the benzene ring in spite that the ionization potential of a silacyclopentadiene ring (for example, 8.20 eV for 1,1,3,4-tetramethyl-1-silacyclopentadiene **1d**)6) is far lower than that of benzene (9.25 eV).13) **1d** formed an orange charge-transfer complex with 5, while benzene did not. Furthermore, we calculated molecular orbitals of **1a** by the CNDO/2 method and the result indicates that the lobe of HOMO is located preferentially on the silacyclopentadiene unit and the contribution from the benzene rings is relatively small. Apparently, the electronic effect is not dominant and the steric effect seems to play an important role in determining the position of 5. Two methyl groups on the silicon atom inhibit 5 from overlapping with the silacyclopentadiene ring. In addition, the structure that two fluoranil molecules overlap with both the benzene rings is preferable from the viewpoint of packing in the crystal lattice since the molecular size of 5 is about one-half of that of **1a**. Therefore, the roles of the silacyclopentadiene and the benzene rings of **1a** are

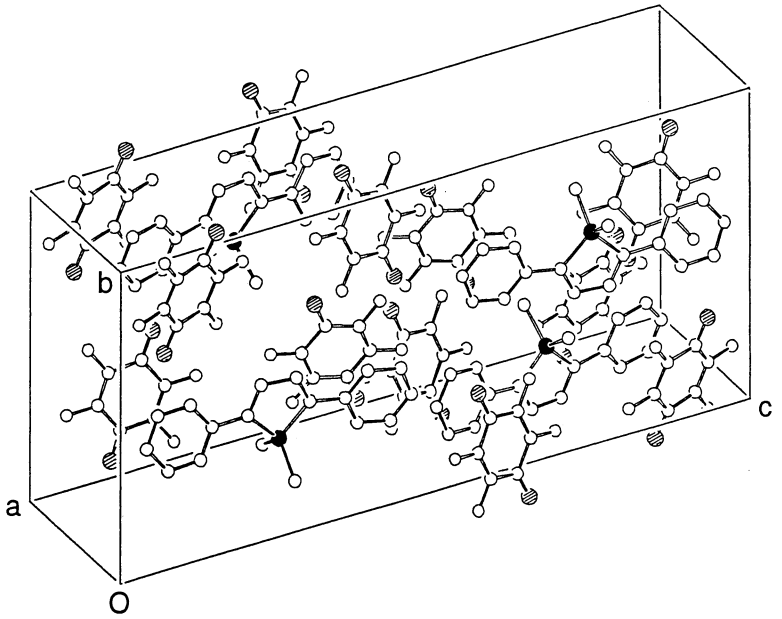

Fig. 3. View of the molecular packing of the **1a**-5 complex. The oxygen atoms in 5 are distinguished with the shades. The filled circles denote silicon atoms in **1a**. H atoms are omitted for clarity.

deduced. The silacyclopentadiene ring lowers the ionization and oxidation potentials of **1a** and increases the electron-donating ability of **1a**, while the benzene rings offer the positions where the quinones can overlap.

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9) In cyclic voltammetry, the oxidation of **1a-c** is an irreversible process and only peak potentials (E_p^{ox}) were obtained. These values were measured vs. SCE in acetonitrile with tetraethylammonium perchlorate as a supporting electrolyte.

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12) Crystal data: $C_{18}H_{18}Si\cdot 2C_6F_4O_2$, Fw = 622.54, orthorhombic, space group Pbcn, a = 7.134(1), b = 13.586(4), c = 28.675(5) Å, V = 2779(1) Å^3, F(000) = 1264, Z = 4, D_c = 1.488 g cm^{-3}, μ(Mo-Kα) = 1.67 cm^{-1}. Data were collected on a Rigaku AFC-4 diffractometer with Mo-Kα radiation (λ = 0.71069 Å). 3371 unique reflections were obtained in the range of $2<2\theta<55°$, and 1217 observed data were used for refinement ($F>3\sigma(F)$). The structure was solved by direct methods using MULTAN78[14)] and successive Fourier syntheses and refined by the block-diagonal least-squares method using UNICSIII[15)] to give R = 0.094. Hydrogen atoms were introduced by difference synthesis.

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