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Electronic Structures and Redox Properties of Silylmethylated C_{60}

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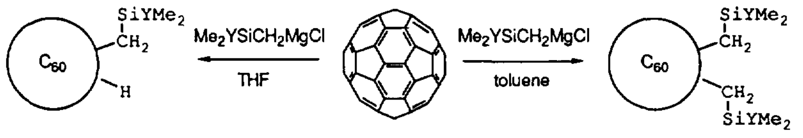
Abstract: Theoretical and electrochemical studies were performed to understand the electronic structure and the redox property of two types of silylmethylated C_{60}, $C_{60}(H)(CH_2SiMe_2Y)$ (**1**) and $C_{60}(CH_2SiMe_2Y)_2$ (**2**) [Y = alkyl, aryl, OR, F]. Semi-empirical molecular orbital (MO) calculations for **1a** (Y = Me of **1**) and **2a** (Y = Me of **2**), and their model compounds, $C_{60}(H)(Me)$ (**3**) and $C_{60}(Me)_2$ (**4**) revealed the thermodynamically most stable isomer of each compound. Cyclic voltammograms showed three to five reversible reduction waves and a quasi-reversible oxidation wave; the redox potentials are consistent with those expected from frontier orbital energies calculated by AM1. Copyright © 1996 Elsevier Science Ltd

Introduction

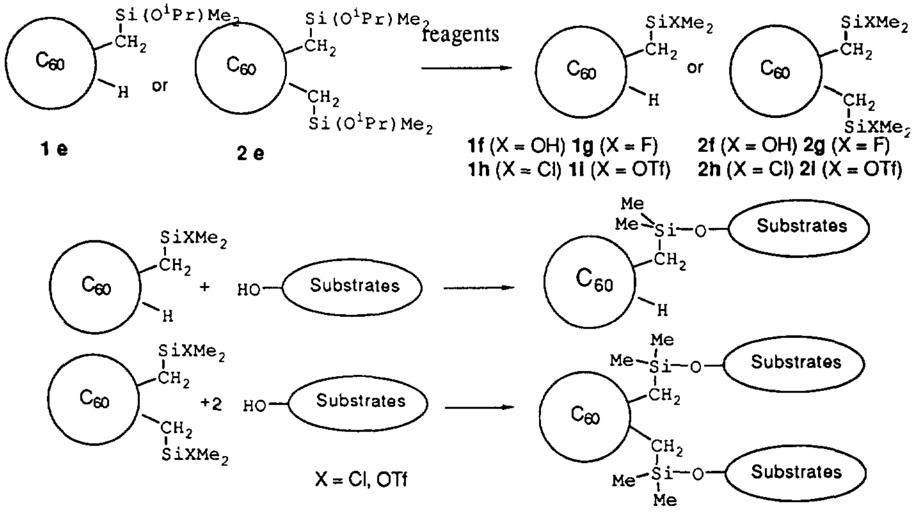
Since a discovery of the Krächmer-Huffman technique for production of massive amounts of fullerenes,[1] numerous reports have been published to yield a number of interesting aspects in their physics and chemistry.[2] In particular, high chemical reactivity of fullerenes has accomplished an access to several types of derivatives with functional groups; this actually has resulted in the discovery of compounds with novel properties and potentially useful applications which had not been achieved with the unmodified fullerenes.[3] Good examples are synthesis of water-soluble fullerene derivatives leading to biological activity[4] and production of fullerene-containing polymers retaining a redox property characteristic to fullerenes.[5]

Addition of organolithium or Grignard reagents to C_{60} was first commented by Wudl at an early stage of fullerene research.[6] After a while, two groups investigated the reaction of C_{60} with ^tBuLi in detail, and the 1 : 1 adduct, $C_{60}(^tBu)Li$, and its protonated compound, $C_{60}(^tBu)H$, were isolated and characterized.[7,8] These results suggest that the addition of organometallic reagents to fullerenes could be a useful method to synthesize various fullerene derivatives. It is attractive from synthetic view-points that a wide variety of organolithium or Grignard reagents with various structures and functional groups are easily available from the corresponding organic halides. In particular, Grignard reagents $ClMgCH_2SiMe_2Y$ are unique in the following points. First, alkyl, aryl, and O^iPr groups can be used as the substituent Y, through which chemical properties of the fullerene adducts can be altered. Second, organosilyl groups are widely used in organic synthesis as a key functional group for further chemical modification.[9] For example, use of the Grignard reagents having aryl or O^iPr group as Y results in the production of the adduct bearing the CH_2SiMe_2Y group on the fullerene surface, which can be transformed to other fullerene derivatives by way of chemical modification of the substituent Y on the silicon atom. The third reason comes from our experience in the transition metal catalyzed coupling of Grignard reagents with diketene, in which marked enhancement in reactivity was observed for $ClMgCH_2SiMe_2Y$ compared with other alkyl or aryl Grignard reagents.[10] It has recently been rationalized both theoretically and experimentally that the organosilyl group at the α-position effectively stabilized the anion, which may provide unusual reactivity in the addition of $ClMgCH_2SiMe_2Y$ to fullerenes.[11]

The results were fruitful as shown in Scheme 1.[12] The reaction of $ClMgCH_2SiMe_2Y$ with C_{60} in THF followed by protonation afforded the 1 : 1 adduct $C_{60}(H)(CH_2SiMe_2Y)$ (**1**), where Y = alkyl, aryl, O^iPr, as the major product. These adducts are a homologue of the known compound, $C_{60}(H)(^tBu)$.[7,8] To our



Scheme 1. Silylmethylations of C_{60}
(Y of **1**, **2**: **a**; Me, **b**; H, **c**; Ph, **d**; $CH=CH_2$, **e**; O^iPr)



Scheme 2. Chemical transformation of silylmethylated C_{60}
(Substrates = organic groups such as alkyl, aryl and inorganic materials such as silica)

surprise, the reaction in toluene produced a different compound from **1** as the major product. The product was assigned as **2**, $C_{60}(CH_2SiMe_2Y)_2$, from spectroscopic evidence, which was a rare example of dialkyl fullerenes.[13] Since the addition of several RLi or RMgX to C_{60} under similar conditions (benzene was used as the solvent) afforded the product, $C_{60}(H)(R)$,[7,8] special reactivity of α-silyl anions, which is difficult to explain now, seems to contribute to the formation of **2**. Since Y of the Gringard reagents $ClMgCH_2SiMe_2Y$ can be altered variously, several organosilylfullerenes were actually synthesized this way. It is noteworthy that the fullerene adducts having ^iPrO group, **1e** and **2e**, can be used as a starting material to synthesize the corresponding fluoride, chloride, and triflate; the latter two compounds are particularly important in the fact that they easily reacted with alcohols, phenols, and even silicas to give many different organic and inorganic fullerene derivatives as shown in Scheme 2.[14]

A wide variety of silylmethylated fullerenes are thus in our hand. Next step should be successful planning of new molecules with interesting properties by these methods. For this purpose, understanding of the structures and electronic properties of the silylmethylated fullerenes is of extreme importance. In this paper, we summarize our studies on electronic structures and redox properties of silylmethylated fullerenes by theoretical and electrochemical investigations.

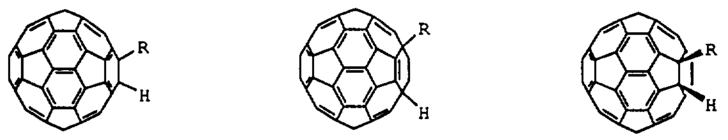
Results and Discussion

Theoretical study.

Semi-empirical calculations of $C_{60}X_2$ [X = H, F, Cl, Br, I] were systematically carried out by Dixon and coworkers, who proposed basic principles for understanding the relative energy of 23 possible isomers.[15] In particular, $C_{60}H_2$ is a good model for **1** and **2**. In contrast to the canonical Kekulé structure of C_{60}, in which all of carbon-carbon double bonds exist in six-membered rings, 22 isomers of $C_{60}X_2$ have at least one double bond placed into a five membered ring. The number of the double bonds in the five membered ring, which corresponds to the number of bond alterations to obtain the Kekulé structure, clearly affords a linear relationship against the calculated ΔH_f°. Consequently, there are two low-energy isomers, that generated by addition of X_2 across the double bond at the junction of two six-membered rings (bond alteration= 0; denoted as [6,6]) and that obtained by 1,4-addition to a six-membered ring(bond alteration = 1; denoted as [1,4]), and the former is generally the most stable isomer. The other isomer which should be mentioned related to the structure of silylmethylated C_{60} is the one generated by addition of X_2 across the double bond at the junction of a five and a six membered rings (bond alteration = 2; denoted as [5,6]). This isomer is less stable than the [6,6]- and [1,4]-isomers. Similar calculations of $C_{60}H_2$ were also reported by Cahill and coworkers.[16,17] These results could be adopted for consideration of the relative energy among isomers of silylmethylated fullerenes.

The structure of **1** was determined by NMR as reported earlier;[12] 32 ^{13}C resonances and a significant NOE intensity enhancement observed between C_{60}-*H* and $C_{60}CH_2Si$ in ^1H NMR were characteristic for the [6.6]-isomer. Similar spectroscopic data for $C_{60}(^tBu)(H)$ were reported by Fagan[7] and Hirsch.[8] In contrast, the structure of **2** remained obscure. Similar to the ^{13}C NMR of **1**, 32 ^{13}C resonances appeared in that of **2**, indicating the existence of the *Cs* symmetry of the molecule. This excluded [6,6]-isomer of **2**, which was expected to give 17 carbon resonances derived from the C_{2v} symmetry of the molecule. It was discovered that hydrolysis of the derivative **2e** gave a cyclic siloxane, $C_{60}(CH_2Me_2Si)_2O$ (**2j**); this means that two of the silyl groups must be closely spaced enough to make the siloxane ring. Only two isomers, **2**-[1, 4] and **2**-[5, 6], are consistent with these spectroscopic and experimental evidence.

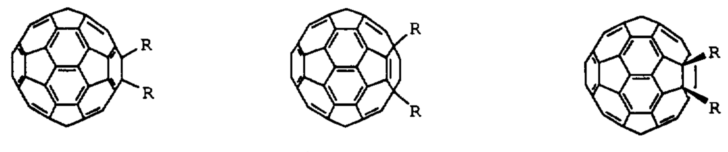
Dixon's calculations on $C_{60}H_2$ suggest that the ground state of the [6,6]-, [1,4]-, and [5, 6]-isomers would be a closed-shell singlet, and they are three of the four compounds with the lowest energies. They also pointed out the following: there is an eclipsing interaction between the substituents in the [6,6]-isomer ([5,6]-isomer, too), the [1,4]-isomer may become more stable than the others when the steric bulk of the substituents is large, and AM1 calculations more precisely estimate the non-bonded interaction than PM3 or MNDO calculations. The ΔH_f° data of $C_{60}(H)(CH_3)$ (**3**)[18] and $C_{60}(CH_3)_2$ (**4**) were calculated by AM1 methods as theoretical models for **1** and **2** (Table 1). The energies of three isomers of **3** decreased in the order, **3**-[5,6] > **3**-[1,4] > **3**-[6,6] ; this trend is similar to that of $C_{60}H_2$.[15-17] In contrast, the [1,4]-isomer was the lowest energy isomer of **4** among the three isomers. The [5,6]-isomer of **4** was higher in energy by ca. 18 kcal / mol than **4**-[1,4]. Similar results were obtained in AM1 calculations of $C_{60}(H)(CH_2SiMe_3)$ (**1a**) and $C_{60}(CH_2SiMe_3)_2$ (**2a**); the isomer with the lowest energy was **1a**-[6,6] and **2a**-[1,4], respectively. The energy difference between the [5,6]-isomer and [1,4]-isomer of **2a** was 13 kcal / mol. These results revealed that the experimentally obtained **1**-[6,6] was the thermodynamically most stable isomer, and may be applied by analogy to the problem of which was formed between the [1,4]- and [5,6]-isomer of **2**. It was also suggested that more stable **2**-[1,4] would be more appropriate for the experimentally obtained product than **2**-[5,6]. Since the formation mechanism of **2** is not clear at present, we cannot completely exclude a possibility that the reaction was controlled kinetically and the less stable **2**-[5,6] was selectively formed. However, it is not very likely that the large energy difference (>10 kcal / mol) between **2**-[1,4] and **2**-[5,6] could make such kinetically controlled reaction possible. Similar results were also obtained with PM3 as shown in Table 1.



R=CH$_3$ (**3**-[6,6])
R=CH$_2$SiMe$_3$ (**1a**-[6,6])

R=CH$_3$ (**3**-[1,4])
R=CH$_2$SiMe$_3$ (**1a**-[1,4])

R=CH$_3$ (**3**-[5,6])
R=CH$_2$SiMe$_3$ (**1a**-[5,6])



R=CH$_3$ (**4**-[6,6])
R=CH$_2$SiMe$_3$ (**2a**-[6,6])

R=CH$_3$ (**4**-[1,4])
R=CH$_2$SiMe$_3$ (**2a**-[1,4])

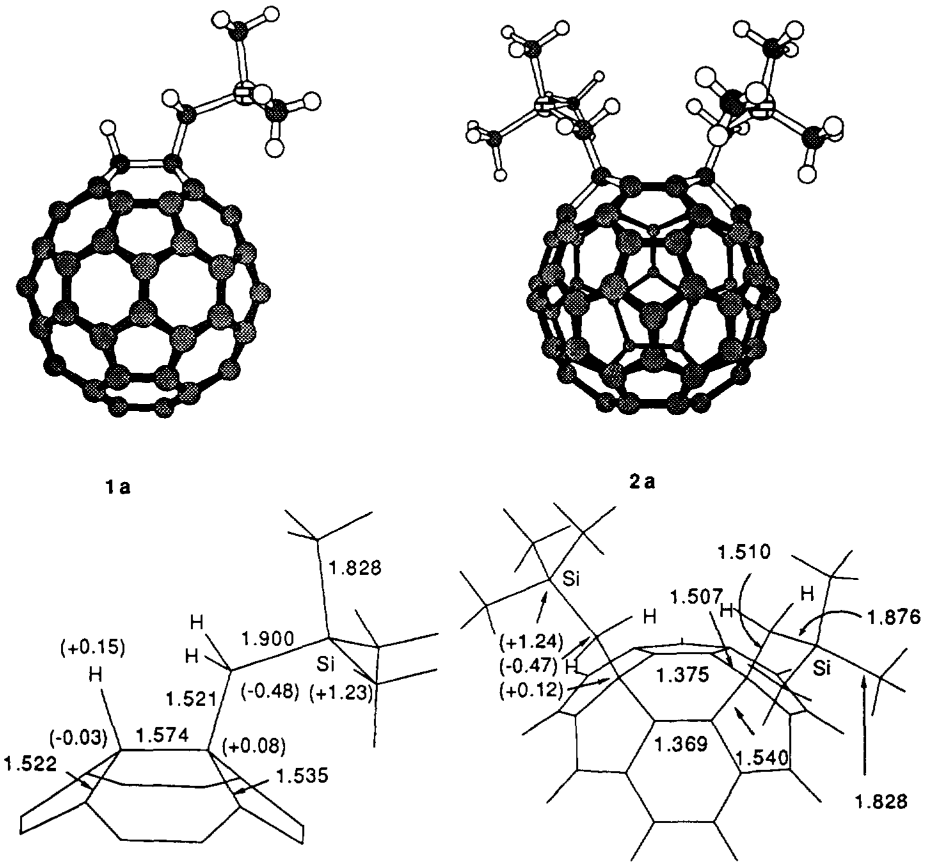
R=CH$_3$ (**4**-[5,6])
R=CH$_2$SiMe$_3$ (**2a**-[5,6])

Figure 1. Calculated molecules.

The optimized structures of 1a-[6,6] and 2a-[1,4] obtained by AM1 calculations including their selected bond lengths and atomic charges are illustrated in Figure 2. It is well known that there are two types of bonds in C$_{60}$, a long bond at the [5,6]-junction and a short bond at the [6,6]-junction. The adduct **1a**-[6,6] resulted from the addition of a proton and a trimethylsilylmethyl group to a short bond, by which two carbons connected to these addenda become close to sp^3. The bond distances around these sp^3-like carbons are 1.52 - 1.57 Å, which are longer than the corresponding bond lengths in C$_{60}$ by ca. 0.1 Å; this furnishes deviation of these carbons from the spherical structure of C$_{60}$. The deviations from the spherical structure are often observed in crystal structures of transition metal complexes of C$_{60}$.[2a,2b] Similar deformation of the carbons attached to the trimethylsilylmethyl groups is also observed in **2a**-[1,4], providing a structure like a cat face with two large ears as shown in Figure 2. Calculated electron density of **1a** or **2a** is essentially similar to **3** or **4**, respectively, except polarization of a carbon-silicon bond which gives rise to relatively larger charges in the methylene carbon of the trimethylsilylmethyl group. Characteristic deshielding of a proton on the C$_{60}$ core in **1a** was in accord with a positive Mulliken charge as noted in the AM1 calculation of **3** by Hirsch et al.[8a]

Orbital energies of the methyl and trimethylsilylmethyl adducts calculated by AM1 are listed in Table 2. The calculations of the three isomers in each compound revealed that the [5,6]-isomer was in general different in its orbital energies from the [1,4]- and [6,6]-isomer.[20] The orbital energies of [1,4]- and [6,6]-isomers were similar in all of the compounds; for example, HOMO and LUMO energies are -9.20 and -2.75 eV with an error of ±0.1 eV. Comparison of methyl compounds **3** or **4** with trimethylsilylmethyl derivatives **1a** and **2a** showed that there is little influence of the trimethylsilyl group in orbital energies. Similar results were also obtained with PM3 calculations.

It is well-known that C$_{60}$ is a good electron acceptor; this was predicted theoretically by a LUMO with low energy level,[21] and supported by many experimental results.[22] The HOMOs with relatively high energy levels are also a characteristic feature of C$_{60}$; however, only a little experimental evidence to suggest that C$_{60}$ acts as a good electron donor is available so far.[2e,22] The HOMO energies of **3**, **4**, **1a**, and **2a** are 0.4-0.5 eV higher in energy than C$_{60}$, whereas their LUMO energies are approximately 0.2 eV higher. These results suggest that the electron affinity of these derivatives is somewhat lower than C$_{60}$, but is still in a range that this molecule is an electron acceptor. In contrast, the derivatives are expected to be a better electron donor than C$_{60}$. Experimental support for these predicted electronic properties were carried out by electrochemical method as described below.



1a

2a

Figure2. Optimized structures, selected bond lengths and atomic charges (figures in parenthesies) of **1a** and **2a**.

Table 1. Calculated ΔH_f°s (AM1 and PM3; kcal / mol).

	AM1	PM3
3-[6,6]	928.5	770.6
3-[1,4]	932.5	774.3
3-[5,6]	945.0	788.6
4-[6,6]	930.2	769.6
4-[1,4]	929.9	769.1
4-[5,6]	947.8	786.7
1a-[6,6]	892.9	733.7
1a-[1,4]	895.5	736.1
1a-[5,6]	911.1	749.1
2a-[6,6]	863.4	697.4
2a-[1,4]	855.7	692.5
2a-[5,6]	878.2	713.5

Table 2. Calculated HOMO and LUMO energies (AM1; PM3: eV)

	NXHOMO	HOMO	LUMO	NXLUMO
3-[6,6]	-9.44; -9.31	-9.24; -9.12	-2.82; -2.79	-2.70; -2.68
3-[1,4]	-9.41; -9.29	-9.22; -9.13	-2.77; -2.78	-2.75; -2.68
3-[5,6]	-9.42; -9.29	-8.92; -8.81	-3.02; -2.98	-2.78; -2.76
4-[6,6]	-9.42; -9.29	-9.22; -9.11	-2.80; -2.78	-2.68; -2.66
4-[1,4]	-9.38; -9.27	-9.24; -9.14	-2.75; -2.96	-2.73; -2.71
4-[5,6]	-9.39; -9.28	-8.90; -8.82	-3.00; -2.96	-2.76; -2.75
1a-[6,6]	-9.40; -9.25	-9.20; -9.07	-2.79; -2.74	-2.66; -2.62
1a-[1,4]	-9.37; -9.23	-9.20; -9.07	-2.74; -2.71	-2.71; -2.67
1a-[5,6]	-9.37; -9.22	-8.85; -8.71	-2.96; -2.88	-2.74; -2.55
2a-[6,6]	-9.33; -9.18	-9.13; -8.98	-2.73; -2.68	-2.56; -2.55
2a-[1,4]	-9.31; -9.16	-9.17; -9.02	-2.69; -2.65	-2.66; -2.61
2a-[5,6]	-9.31; -9.16	-8.82; -8.67	-2.91; -2.83	-2.70; -2.66
C_{60}		-9.64[a]; -9.48[c]	-2.95[b]; -2.89[c]	

a) The HOMO is five-fold degenerate. b) The LUMO is three-fold degenerate. c) The values are coincidence with those reported in ref. 15a.

Electrochemical Studies.

Electrochemistry has been playing an important role in fullerene science.[22] In fact, cyclic voltammetry of C_{60} and C_{70} first provided an experimental verification of initial molecular-orbital calculations suggesting that they would exhibit the chemistry of electron-deficient molecules. Electrochemical measurement of fullerene derivatives have also received much attention from chemists in seeing changes of electronic properties by attachment of organic or inorganic addenda on the surface of fullerenes[23-24] or encapsulation of metals into the carbon cage.[25] In particular, Suzuki and coworkers reported redox properties of some of organofullerenes, of which redox potentials were well correlated with their frontier orbital energies calculated by AM1.[23]

Cyclic voltammograms of silylmethylated fullerenes were obtained in 1,2-dichlorobenzene at room temperature. As typical examples, those of **1c** and **2c** are shown in Figure 3. Upon reduction, three reversible waves appeared, which can be assigned to the formation of their monoanion, dianion, and trianion, respectively. Similar results were obtained for other silylmethylated C_{60} species, and their reversible half-wave potentials (E1, E2, and E3) are listed in Table 3. The values of E1, E2, and E3 were independent of the substituent on the silicon atom. No essential difference was observed for the potentials between monosilylmethylated compounds **1** and disilylmethylated compounds **2**.[26] Each of reduction potentials is shifted 0.1 - 0.2 V to more negative potentials relative to C_{60}. As described above, AM1 calculations revealed that the energy level of the LUMO of **1a** or **2a** was approximately 0.2 eV higher than that of C_{60}. According to the Suzuki's correlation diagram of the energy level of the LUMO vs reduction potentials observed in 1,2-dichlorobenzene, compounds having the calculated LUMO levels were expected to give the first and second reduction potentials at -1.1 and -1.5 V, respectively, which were identical with the actual potentials we obtained. Little difference in MO energy levels between **1a** and **2a** suggests that they would give similar reduction potentials; this is in accord with the experimental results. There is a possibility that substituents on the silicon atom may affect the redox potentials by way of through-bond or through-space interaction. As indicated by the data we obtained, such special interaction was not visible. An irreversible signal seen in the voltammogram of **1c** at -0.6V, which is generally observed for the monosilylmethylated C_{60}, will be discussed later.

It is known that the six known reductions of C_{60} have all been found to be reversible by cyclic voltammetry at -10°C; this is consistent with initial MO calculations of C_{60} predicting a triply

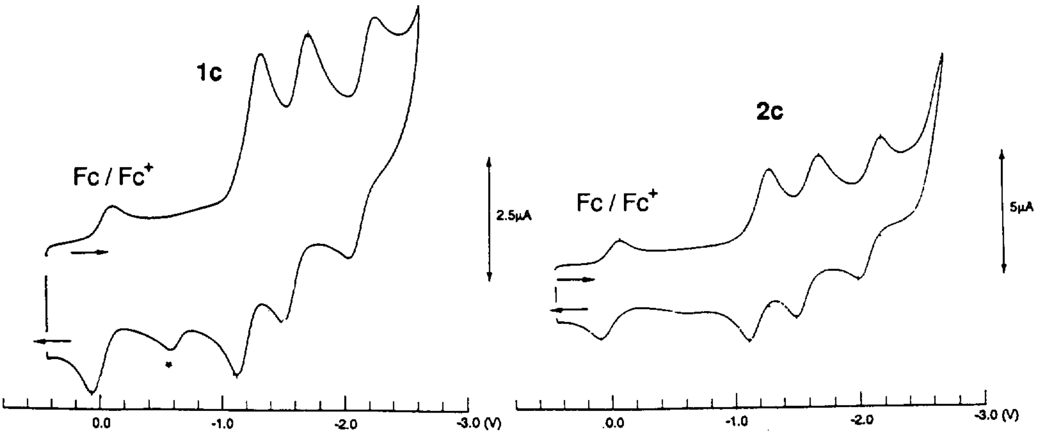


Figure 3. Cyclic voltammograms of **1c** and **2c** (0.4 mM).

Table 3. Reversible potentials for silylmethylated fullerenes in 1,2-dichlorobenzene at room temperature.[a]

	E1	E2	E3
1a (Y = Me)	-1.25	-1.61	-2.16
1b (Y = H)	-1.23	-1.60	-2.12
1c (Y = Ph)	-1.22	-1.61	-2.15
1d (Y = $CH=CH_2$)	-1.24	-1.63	-2.15
1e (Y = O^iPr)	-1.24	-1.60	-2.13
1f (Y = OH)	-1.27	-1.59	-2.13
1g (Y = F)	-1.22	-1.62	-2.13
2a (Y = Me)	-1.25	-1.65	-2.16
2c (Y = Ph)	-1.23	-1.62	-2.12
2d (Y = $CH=CH_2$)	-1.22	-1.62	-2.13
2e (Y = O^iPr)	-1.23	-1.62	-2.11
2j[b]	-1.24	-1.62	-2.12
C_{60}	-1.12	-1.48	-2.00

a) V vs ferrocene / ferrocenium couple. 0.07M $(n\text{-}Bu)_4N^+PF_6^-$ was used as a supporting electrolyte. Scan rate was 0.20V / s. The values reported are the reversible voltammetric half-wave potentials. Experimental error = ±0.02V.b. A cyclic siloxane; the [1,4]-isomer of $C_{60}(CH_2SiMe_2)_2O$.

degenerate LUMO of t_{1u} symmetry.[27] Selection of the solvent and rigorous exclusion of moisture and air are important for the detection of all of the six reduction processes. Four silylmethylated fullerenes, **1c**, **1e**, **2c**, and **2e** were subjected to the electrochemical measurement using a cell connected to a vacuum line. A mixture of toluene and acetonitrile was used as the solvent, which was used for detection of the sixth reduction wave by Echegoyen and coworkers.[27] As shown in Figure 4, the forth reduction wave was clearly visible in cyclic voltammograms of **1e** or **2e**. In the case of **1e**, the fifth reduction wave was also seen as a quasi-reversible wave at -3.34 V. Each reduction is electrochemically reversible and each involves the transfer of one electron. The reduction potentials for the first and second waves are 0.1 V lower than those for C_{60}, whereas the third and the forth reduction waves are 0.2V shifted to more negative potentials. Detection of four reversible reduction waves means facile four electron reduction of silylmethylated fullerenes; this corresponds to existence of a NXLUMO at a close energy level to the LUMO, which is consistent with the theoretical results described above.

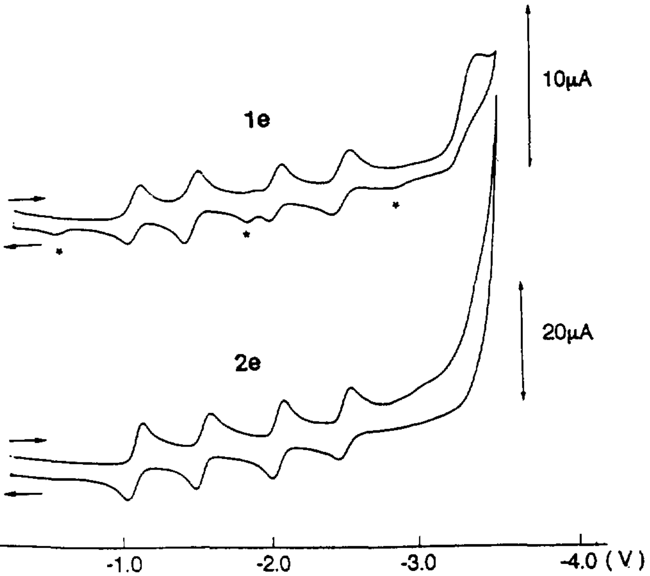


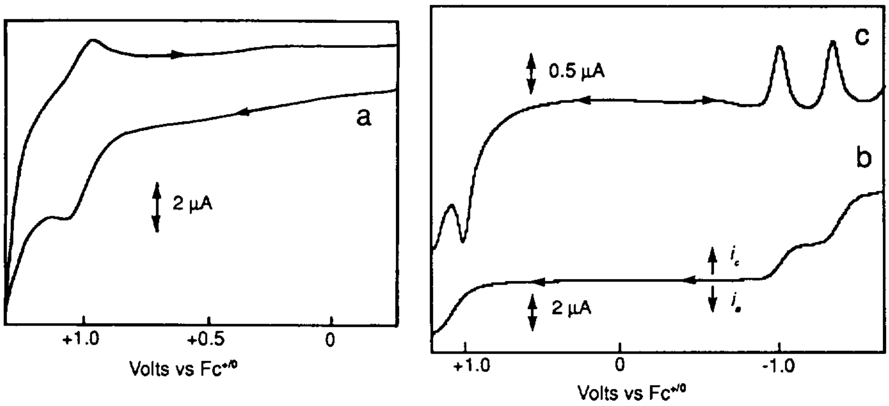
Figure 4. Cyclic voltammograms of **1e** and **2e** in toluene-acetonitrile.

Table 4. Reversible potentials for silylmethylfullerenes in toluene-acetonitrile at -20°C under unaerobic conditions.[a]

	E1	E2	E3	E4	E5	E6
1c(Y = Ph)	-1.10	-1.49	-2.06	-2.49	-3.34	--
1e(Y = O^{i}Pr)	-1.11	-1.49	-2.06	-2.52	-3.34	--
2c(Y = Ph)	-1.09	-1.51	-2.05	-2.51	--	--
2e(Y = O^{i}Pr)	-1.09	-1.52	-2.05	-2.51	--	--
2j^c	-1.09	-1.52	-2.06	-2.51	--	--
C_{60}	-0.98(-0.98)^b	-1.36(-1.37)^b	-1.86(-1.87)	-2.34(-2.35)	-2.85(-2.85)	-3.34(-3.26)

a) V vs ferrocene / ferrocenium couple. 0.1M $(n\text{-}Bu)_4N^+PF_6^-$ was used as a supporting electrolyte. Scan rate was 0.05V / s. The values reported are the reversible voltammetric half-wave potentials. Experimental error = ±0.02V. b) The values in parenthesis are those reported in literature. c) A cyclic siloxane; the [1,4]-isomer of $C_{60}(CH_2SiMe_2)_2O$.

A difference between cyclic voltammograms of monosilylmethylated and disilylmethylated derivatives in 1,2-dichlorobenzene is the existence of an irreversible oxidation peak at -0.6V. Similarly, cyclic voltammograms of **1c** and **1e** in toluene-acetonitrile showed several small irreversible waves. Typical examples are shown in Figure 4; the irreversible peaks are indicated with an asterisk. Since there was no irreversible peak in the cyclic voltammograms of **2**, they would be derived from chemical reactions of the proton bonded to the C_{60} moiety in **1**. Electrochemical studies on $C_{60}H_2$ have been extensively performed in the last two years.[28] Kadish and coworkers reported that the $C_{60}H_2$ undergoes four reversible reductions in a mixture of toluene and DMF, and the products of the first two reductions are stable on the cyclic voltammetric time scale while those of the third and fourth are unstable and decompose to give the parent C_{60}.[28a] Detailed studies on the electrochemical reduction of **1e** in 1,2-dichlorobenzene revealed that the first reduction product was stable, whereas the second reduction gave a product showing the irreversible wave at -0.6 V. When the potential was held at a slightly more negative potential than the second wave for 30 sec during the scan, current of the irreversible peak was apparently increased. A possible chemical reaction to give the irreversible peak is deprotonation. It is known that a proton bound to C_{60} is highly acidic; that of $C_{60}(H)(^tBu)$



Cyclic (a), rotating disk (b), and differential pulse voltammograms (c) of **1c** at a Pt electrode in 1,2-dichlorobenzene. (a) scan rate = 1 V / s. (b, c) scan rate = 20 mV / s. (b) pulse width = 50 mV.

Figure 5. Detection of oxidation waves by cyclic voltammetry of **1c**.

was easily deprotonated even with an acetate anion.[7] Reversible potential for the ${}^{t}BuC_{60}^{\bullet}$ / ${}^{t}BuC_{60}^{-}$ was -0.33 V vs Fc / Fc$^+$.[7] Analogous anionic species $Me_2YSiCH_2C_{60}^{-}$ may be formed by the reaction of electrochemically generated anionic species such as $(Me_2YSiCH_2C_{60}H)^{n-}$ ($n > 1$) with neutral $Me_2YSiCH_2C_{60}H$ in the cyclic voltammetric time scale, affording a irreversible wave around -0.6 V. Similarly, irreversible peaks observed at the more negative potentials in the cyclic voltammograms in toluene-acetonitrile would be derived from deprotonated species of $(Me_2YSiCH_2C_{60}H)^{n-}$.

Electrochemical detection of C_{60}^{+} is more difficult than that of anionic species.[21,29] In many solvents, the oxidation process is irreversible, and a reversible oxidation wave was available only in tetrachloroethane.[29b] Interestingly, silylmethylated fullerenes, **1c**, **1e**, **2c**, and **2e** gave quasi-reversible oxidation waves around +1.10 V vs Fc / Fc$^+$ couple in 1,2-dichlorobenzene (**1c**; +1.10 V, **1e**; +1.10 V, **2c**; +1.05 V, and **2e**; +1.12 V). At the lower scan rate, the reversiblility became poor and only an oxidation peak was observed. The best voltammogram was available for **1c** as shown in Figure 5. The limiting current of the oxidation process in a rotating disc voltammogram shows almost the same height as that of the first or the second reduction process, which strongly suggests the one-electron process for the oxidation. Although electrochemical oxidation of several organofullerenes was carried out by Suzuki and coworkers, they reported that the oxidation process was irreversible in all cases.[23] It is well-known that polarization of carbon-silicon bonds effectively stabilized a cationic species at β-carbon of the organosilyl group, leading to rich chemistry of allyl, vinyl, or arylsilanes.[9] Detection of reversible oxidation waves for silylmethylated fullerenes may be attributed to stabilization of fullerenium ions by triorganosilylmethyl group bonded to the C_{60} cage. Suzuki's analysis of oxidation potentials of organofullerenes was performed using peak potentials by DPV.[23] The oxidation wave of C_{60} appeared at +1.26 V in 1,2-dichlorobenzene, which is approximately 0.2 V higher than that of **1c**. This apparently suggests that oxidation of silylmethylated fullerenes is easier than that of C_{60}. The higher HOMO level of silylmethylated fullerenes than that of C_{60} described above is consistent with these experimental results.

Conclusion

Above results revealed the following; first, it was concluded from spectral evidence and AM1 calculations that the the products obtained by silylmethylation of C_{60} would be the [6,6]-isomer of **1** and the [1,4]-isomer of **2**, of which optimized structures were proposed as shown in Figure 2. Second, calculated orbital energies predicted that silylmethylated fullerenes were worse electron acceptors and better electron donors than C_{60}. These predictions were acturally proved by electrochemical methods. Semi-empirical MO calculations and electrochemical measurements, either one or both have taken part in understanding structures and electronic properties of fullerenes and their derivatives.[1,2,21] As related work, we should refer to publications by Hirsch,[8a] Fagan and Evans,[22b] and Kadish,[13] who reported AM1 calculations of $C_{60}(Me)H$, electrochemical studies of $C_{60}(^tBu)(Me)$, and electrochemical studies of $C_{60}(CH_3)_2$, respectively. Electronic properties depicted for these compounds are essentially similar to our results on the silylmethylated C_{60}. Thus, organosilyl groups in silylmethylated C_{60} themselves do not affect the electronic properties of the compounds. As described earlier, silylmethyl groups effectively contribute to linking the C_{60} moieties to various organic and inorganic groups. We have established synthetic methods of two types of silylmethylated fullerenes **1** or **2** by Grignard addition reactions. The silylmethyl magnesium reagents having alkyl, aryl, vinyl, or alkoxy groups on the silicon atom can be used for the reaction; this means that the CH_2Me_2Si moiety act as a bridge between these groups with the C_{60} cage. Replacement of the ^iPrO groups in **1e** or **2e** by alcohols and phenols have provided a general way linking the C_{60} moieties to organic groups in alcohols and phenols through silicon-oxygen bonds. An interesting application of this replacement reaction is attachment of $C_{60}(H)CH_2Me_2Si$ group to surface of silica; this modified silica has proven to be useful as a unique stationary phase of micro-column HPLC, which can effectively separate fullerenes and or polyaromatic hydrocarbons.[14] From a view of synthetic planning of novel fullerene molecules, these processes offer a general way to introduce "fullerenomethylsilyl groups" to various organic or inorganic moieties. Theoretical and electrochemical studies presented in this paper contribute to understanding geometrical or electronic nature of the "fullerenomethylsilyl groups", so that chemists could have real images what will happen to connect any desired organic or inorganic materials to C_{60} moieties through CH_2Me_2Si or CH_2Me_2SiO groups. This work was supported by a grant from the Ministry of Education, Science, and Culture of the Japanese Government (0523105).

Experimental

Semi-empirical calculations were done with the program system MOPAC ver.6 with the MNDO Hamiltonian and the AM1 or PM3 parameterization in the Gaussian 92 package. The geometry optimization was performed with the PRECISE option in MOPAC. Cyclic voltammetric studies were carried out using a potentiostat / galvanostat (Hokuto denko, HAB-151) or a BAS 100 B/W electrochemical analyzer. A platinum disk working electrode, a platinum wire counter electrode, and a silver reference electrode comprised of a silver wire in contact with 0.01 M $AgNO_3$ and 0.2 M $(^nBu)_4N^+PF_6$ in acetonitrile were used for the cyclic voltammetry in 1,2-dichlorobenzene at room temperature. Cyclic voltammetric studies in toluene-acetonitirile were performed using a wire of platinum as both working and counter electrodes and a silver wire as a quasireference. In the cell attached these electrodes were placed a sample, supporting electrolyte, and ferrocene (internal standard). The cell was connected to a vacuum line, and the solvents were distilled under vacuum. Details in each experiment are described in captions of the tables. Preparation of silylmethylated fullerenes was reported elsewhere.[12,14] All of the solvents were distilled over drying reagents (1,2-dichlorobenzene and acetonitrile, P_2O_5; toluene, Na / Ph_2CO). $(^nBu)_4N^+PF_6$ was purified by recrystallization from ethanol.

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20. The HOMO and LUMO energies of the [5,6]-isomers of **1a**, **2a**, **3**, and **4** were comparable to those of C_{60}. If the [5,6]-isomer of **2** was formed experimentally, their redox potentials in cyclic voltammetry should be similar to those of C_{60}. The actural potentials obtained were rather similar to those for **1**; this supports the formation of the [1,4]-isomer of **2**.
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