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Silylation of higher fullerenes†

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Photochemical silylations of higher fullerenes (C_{70}, $C_{76}(D_2)$, $C_{84}(D_2)$) are reported. During the photochemical cycloaddition of these higher fullerenes with disilirane, the formation of mono-adducts was observed. Since the highly selective disilirane addition to C_{70} was observed, the reaction of $C_{76}(D_2)$ and $C_{84}(D_2)$ with disilirane gave at least eight and seven isomers of the mono-adduct, respectively. These adducts were isolated in their pure form by multistage HPLC. The electronic properties of these adducts were also investigated using differential pulse voltammetry. The results indicate that silylation is very effective for producing the electronegative higher fullerene derivatives.

Introduction

During the course of our study on the chemical functionalization of fullerenes with organosilicon compounds, we have already reported the photochemical mono- and bis-silylations of C_{60}[1] and C_{70}.[2] In order to design new organofullerenes for applications in material science and biochemistry, one should know their electronic properties, namely their redox properties. We showed that the reduction and oxidation potentials represent a good linear correlation with the LUMO and HOMO energy levels, respectively, based on a comparative electrochemical study of various organofullerenes derivatised with oxygen-, carbon-, and silicon-containing groups at the 6,6-ring junction.[3] Among them, a characteristic feature of the monosilylated and bissilylated fullerenes is their higher reduction and lower oxidation potentials than C_{60} itself. This result can be confirmed by a theoretical calculation indicating that almost one electron flows into C_{60} from the silicon substituents.[3] It was impressive that silicon derivatives are much more electropositive than their carbon analogs and C_{60}. On the other hand, the higher fullerenes, such as C_{70}, C_{76}, C_{84}, are known to have higher HOMO and lower LUMO levels than those of C_{60}.[4] With the development of the isolation and structure determination of higher fullerenes in recent years, the structure assignments of D_2-C_{76},[5] three isomers (C_{2v}, C'_{2v} and D_3) of C_{78}[6–8] and ten isomers of C_{84}[9–13] were possible. The chemical reactivity of the higher fullerenes has seen increasing attention, and enormous progress has been made. On the basis of the reported results,[14–16] the chemistry of the higher fullerenes significantly differs from that of C_{60}. Therefore it is expected that the silylation of the higher fullerenes will produce silylfullerenes with lower oxidation potentials than the analogous C_{60} derivatives.[1b] In this context, we recently reported the photochemical bis-silylation of $C_{78}(C_{2v})$[17] and $C_{76}(D_2)$.[18] In this paper, we report the redox properties of the silylated higher fullerenes (C_{70}, $C_{76}(D_2)$, $C_{84}(D_2)$).

Experimental section

The higher fullerenes (C_{70}, $C_{76}(D_2)$, $C_{84}(D_2)$) were purified by a previously reported method.[5,9] Their purities were confirmed by HPLC analysis and ^{13}C-NMR measurement.

Cyclic voltammetry (CV) experiments were performed at a 1 mM analyte concentration in 1,2-dichlorobenzene with 0.1 M Bu_4NPF_6, a Ag/$AgNO_3$ (CH_3CN) reference electrode, and a Pt disc working electrode. Ferrocene (0.5 mM) was added as the internal reference. The scan rate was 20 mV s^{-1}. Differential pulse voltammetry (DPV) experiments were carried out under the same conditions as for the CV measurements. The pulse amplitude, pulse width and pulse period were 50 mV, 50 ms and 200 ms, respectively. The scan rate was 20 mV s^{-1}.

The reaction of C_{70} with silylene

A 13 ml solution of C_{70} (26.2 mg, 0.031 mmol) and 2,2-bis(2,6-diisopropylphenyl)hexamethyltrisilane (17.6 mg, 0.040 mmol) as a silylene precursor in toluene was photolyzed with a low-pressure mercury arc lamp for 2 hours, the reaction mixture was injected into the preparative Gel 1H + 2H column during the first stage, and bis(2,6-diisopropylphenyl)silane **2** was isolated along with unreacted C_{70} and the bis-adduct. The two pure adducts (**2a**, **2b**)[2b] were isolated in the second stage using a Buckyprep column.

The reaction of C_{76} with disilirane 3

A 25 ml solution of C_{76} (10 mg, 0.011 mmol) and **3** (12 mg, 0.022 mmol) in toluene was placed in a Pyrex tube degassed by freeze–pump–thaw cycles under reduced pressure, then irradiated with a halogen lamp (cut off < 400 nm) for 24 hours. The reaction mixture was injected into the preparative Gel 1H + 2H column during the first stage. 1,1,3,3-Tetramesityl-1,3-disiloane **9** was isolated in 66% yield with 2% unreacted C_{76} and 10% bis-adduct. The three pure adducts (**9a–c**) were isolated in the second stage using a Buckyprep column and one adduct was isolated in pure form in the third stage by a

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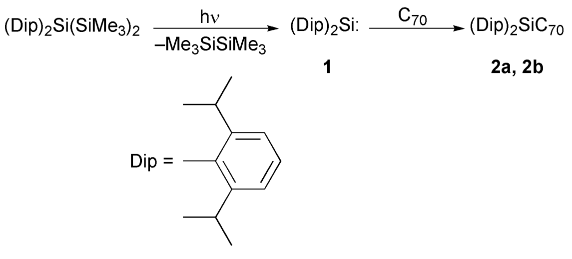
Buckyclutcher column. The four isomers (**9a**–**d**) were isolated with 15.2, 6.2, 4.1 and 13.3% yields.

The reaction of C_{84} with disilirane 3

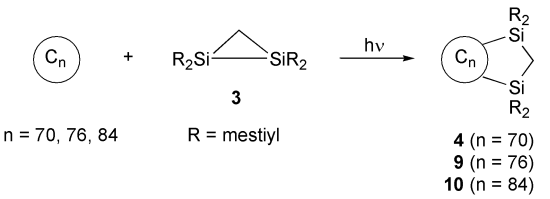
A 40 ml solution of $C_{84}(D_2)$ (16 mg, 0.016 mmol) and **3** (44 mg, 0.08 mmol) in toluene was placed in a Pyrex tube, degassed by freeze–pump–thaw cycles under reduced pressure, then irradiated with a halogen lamp (cut off <4 00 nm) for 5.5 hours. The reaction mixture was injected into the preparative Gel 1H + 2H column during the first stage. 1,1,3,3-Tetramesityl-1,3-disiloane **10** was isolated along with the bis-adduct. The three pure adducts (**10a**–**c**) were isolated in the second stage using a Buckyclutcher column.

Results and discussion

Recently, we reported some interesting redox properties of silylated C_{60}.[3] A characteristic feature of the mono- and bis-silylated C_{60}s is their higher reduction and lower oxidation potentials than those of C_{60} itself and analogous carbon substituted derivatives. This is due to the electron-releasing nature of the silicon relative to carbon. In order to determine the electronic properties of the silylated higher fullerenes, the redox potentials of the adducts were measured by differential pulse voltammetry.



Scheme 1



Scheme 2

A. Syntheses and redox properties of silylated C_{70}

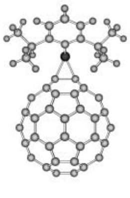
While all the positions in C_{60} are identical, five sets of carbon atoms and eight distinct types of C–C bonds are available in C_{70}. We have reported that C_{70} reacts with photochemically generated silylene **1** to give positional isomeric 1 : 1 adducts (**2a**, **2b**) as isolable products (Scheme 1). The spectroscopic analyses and theoretical investigations strongly support the silylene addition at the a–b (**2a**) and c–c (**2b**) double bonds.[2b] Recently, we succeeded in separating these two isomers using a Buckyprep column. On the other hand, the addition of disilirane to C_{70} affords the bis-silylated adduct **4** (Scheme 2).[2a] We recently reported that disilirane reacts with the triplet excited state of fullerenes to give the adducts[19] and also found a metal free bis-silylation in the reaction of disilirane with C_{60} in PhCN.[20]

The redox properties of C_{70} and its adducts determined by DPV are summarized in Table 1 along with C_{60}, the silylated C_{60} (**5**, **6**, **7**) and the carbon analogue **8** as reference compounds. The three silylated C_{70}s showed very similar redox properties even though the addition positions are different. These results indicate that no significant differences exist between the redox properties of these adducts having different addition positions. Diederich and coworkers also reported that the constitutional isomers of the multi-adducts of C_{70} displayed nearly identical redox properties.[21] As a general trend, the reductions become slightly more difficult, whereas the first oxidation becomes much more facilitated. The redox properties of bis(alkoxycarbonyl)methano-C_{70}(**8**), which is a carbon analogue of **2a**, was also recently reported.[21] It is impressive that the silicon derivative **2a** is even more electropositive than its carbon analogue **8**. These redox characteristics of the C_{70} adducts closely resemble those of the silylated C_{60}s.[1–3]

Table 1 Redox potentials[a] of C_{70}, **2a**, **2d**, C_{60}, **4**, **5**, **6**, **7**, and **8**

Compd.	$^{Ox}E2$	$^{Ox}E\ 1$	$^{Red}E\ 1$	$^{Red}E2$	$^{Red}E3$	$^{Red}E4$	$^{Red}E5$
C_{70}		1.21	−1.10	−1.46	−1.86	−2.27	
2a		0.59	−1.22	−1.59	−2.02		
2b		0.61	−1.24	−1.58	−1.97		
4	1.17	0.61	−1.11	−1.48	−2.03		
C_{60}		1.32	−1.13	−1.50	−1.94	−2.41	
5		0.65	−1.26	−1.63	−2.18		
6[b]	1.23	0.73	−1.35	−1.70	−2.22		
7[c]		0.59	−1.24	−1.63	−2.15		
8[d]		1.12	−1.05	−1.44	−1.84	−2.02	−2.26

[a] Values are in Volts relative to a ferrocene/ferrocenium couple and obtained by DPV. Conditions: 0.1 M (n-Bu)$_4$NPF$_6$ in 1,2-dichlorobenzene, the working electrode and counter electrode are Pt wire, the reference electrode is Ag/0.01 M AgNO$_3$ and 0.1 M (n-Bu)$_4$NCl$_4$ in CH$_3$CN. Pulse width, 50 ms; pulse period, 200 ms; scan rate, 20 mV s^{-1}. [b] ref. 3. [c] ref. 1c. [d] ref. 21.



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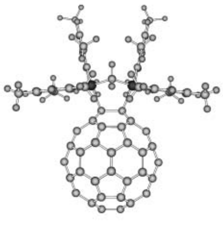

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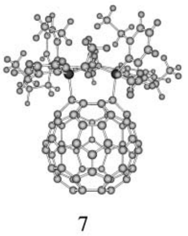

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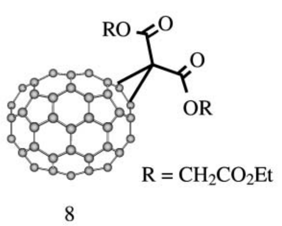

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B. Syntheses and redox properties of silylated C_{76}

Irradiation of a toluene solution of **3** and C_{76} with a halogen–tungsten lamp (cutoff $<$ 400 nm) resulted in the formation of 1,1,3,3-tetramesityl-1,3-disilorane (**9**) in 66% yield. It took 24 h to complete the reaction. This low reactivity might originate from its low triplet quantum yield.[22] After the three-stage HPLC separation, four isomers **9a**–**9d** were isolated in pure form accompanied by at least four isomers, which were not further investigated. The reaction of C_{76} with disilirane **3**, which gave at least eight isomers, is distinct from the reaction of C_{70} with **3**, which resulted in the formation of only one isomer. The symmetries of **9a**–**d** were determined by their ^{1}H and ^{13}C NMR measurements. The ^{1}H NMR spectra of the isomers **9a**–**d** showed twelve methyl signals with equal intensity, and in ^{13}C NMR spectra, 76 signals of fullerene carbons were also observed. These results indicate that these four isomers have C_1 symmetry. The disilirane **3** adds to C_{60} at the 6-6 ring junctions to afford the corresponding 5-membered ring.[1b] It can be assumed that **3** also adds to C_{76} at the 6-6 ring junction. While all the positions in C_{60} are identical, the presence of 19 different C-atoms and 15 different 6-6 bonds gives rise to a large number of possible mono-adduct isomers in C_{76}. Although it is possible to form 15 mono-adduct isomers containing twelve C_1-symmetrical isomers and three C_2-symmetrical isomers, we have succeeded in isolating the four isomers that have C_1 symmetry. At this point, the actual assignment of their isomers, however, awaits X-ray structural determination.

In order to determine the electronic properties of the bis-silylated C_{76}, the redox potentials of **9a**–**d** have been measured by differential pulse voltammetry. Table 2 shows the redox potentials of the adducts (**9a**–**d**) and C_{76} itself.

The salient feature is that **9a**–**d** have a low oxidation potential (+0.62–+0.39 V) compared to C_{76} (+0.73 V) itself. The oxidation of mono-adducts is easier than the parent fullerene, and all four C_{76} mono-adducts undergo the second oxidation step, while the C_{76} only shows one oxidation under the same conditions.

Meanwhile, the reduction potentials of **9a**, **9b** and **9d** relative to C_{76} are cathodically shifted about 150–160 mV, and the reduction of three mono-adducts is more difficult than the parent C_{76}, which indicates that the introduction of a silyl group results in decreasing electron-accepting properties. These findings agree with that previously observed for the other silylfullerenes.[1–3] In contrast, the mono-adduct **9c** is slightly more readily reduced than the parent fullerene (Table 2), which is in sharp contrast to the results obtained for the silylfullerenes. Recently, Diederich *et al.* reported the synthesis and redox properties of three C_{76} derivatives and two of them were more readily reduced than C_{76} and the other was more difficult to oxidize.[21] In our case, one of the four has a slightly lower reduction potential but the others are more difficult to reduce, and all derivatives have much lower oxidation potentials. These results indicate that silylation is very effective for producing the electronegative C_{76} derivatives.

C. Syntheses and redox properties of silylated C_{84}

The reaction of disilirane and C_{84} was carried out by a procedure similar to that described above. According to the reaction time, the reactivity of $C_{84}(D_2)$ is greater than that of C_{76}. After the two-stage HPLC separation, three isomers **10a**–**10c** were isolated in pure form accompanied by at least seven isomers, which were not further investigated. The reaction of C_{84} with disilirane **3**, which gave at least ten isomers, is distinct from the reaction of C_{70} with **3**, which resulted in the formation of only one isomer, but is almost the same as that of C_{76} with disilirane **3**. The symmetries of **10a**–**10c** were determined by their ^{1}H NMR measurements. **10a** and **10c** have C_1 symmetry, but **10b** has C_2 symmetry. There is only one 6,6-bond (C32–C53) which gives the C_2 symmetrical adduct. The disilirane might add to this bond of C_{84} to give **10b**. Further investigations are in progress.

In order to compare the electronic properties of the silylfullerenes, the redox potentials of **10a**–**d** have been measured by differential pulse voltammetry. Table 3 shows the redox potentials of the adducts (**10a**–**c**) and $C_{84}(D_2)$ itself. The two mono-adducts of **10a** and **10b** revealed similar electrochemical properties; two oxidation steps and four reduction steps were observed for the two isomers, and the difference is only 10–20 mV between **10a** and **10b**. On the other hand, **10c** revealed three oxidation steps and five reduction steps. The three isomers have lower oxidation potentials (+0.71–+0.27 V) compared to $C_{84}(D_2)$ (+0.88 V) itself, and the oxidation of the mono-adducts is easier than the parent fullerene, which is consistent with the observations for the other silylfullerenes. Also the **10c** isomer has the lowest oxidation potential (+0.27 V), and the electrochemical gap becomes significantly smaller than that of the parent fullerene or the other two mono-adducts. To our knowledge, **10c** is the easiest to oxidize of all the fullerene derivatives reported previously.

Conclusion

We carried out silylation of the higher fullerenes (C_{70}, $C_{76}(D_2)$, $C_{84}(D_2)$) and isolated the adducts by multistage HPLC separations. The redox properties of the silylated higher fullerenes were investigated by DPV. In general, the silylated higher fullerenes have lower oxidation potentials than the parent fullerenes and analogous C_{60} derivatives. These results indicate that silylation is very effective for producing the electronegatively higher fullerene derivatives. These silicon derivatives might constitute an important stepping stone on the way to material, catalytic, and biological applications.

Table 2 Redox potentials[a] of C_{76} and **9a**–**d**.

Compd.	${}^{Ox}E2$	${}^{Ox}E\ 1$	${}^{Red}E\ 1$	${}^{Red}E2$	${}^{Red}E3$	${}^{Red}E4$
C_{76}		0.73	−1.00	−1.30	−1.76	−2.15
9a	0.78	0.62	−1.15	−1.55	−1.83	−2.44
9b	0.72	0.56	−1.16	−1.47	−1.70	−2.33
9c	0.76	0.53	−0.98	−1.32	−1.65	
9d	0.69	0.39	−1.15	−1.52	−1.97	−2.40

[a] Values are in Volts relative to a ferrocene/ferrocenium couple and obtained by DPV. Conditions: 0.1 M $(n\text{-}Bu)_4NPF_6$ in 1,2-dichlorobenzene, the working electrode and counter electrode are Pt wire, the reference electrode is Ag/0.01 M $AgNO_3$ and 0.1 M $(n\text{-}Bu)_4NClO_4$ in CH_3CN. Pulse width, 50 ms; pulse period, 200 ms; scan rate, 20 mV s^{-1}.

Table 3 Redox potentials[a] $C_{84}(D_2)$, **10a**, **10b** and **10c**

Compd.	${}^{Ox}E3$	${}^{Ox}E2$	${}^{Ox}E\ 1$	${}^{Red}E1$	${}^{Red}E2$	${}^{Red}E3$	${}^{Red}E4$	${}^{Red}E5$
$C_{84}(D_2)$			0.88	0.74	1.03	1.36	1.71	2.47
10a		0.94	0.71	−0.86	−1.18	−1.71	−2.14	
10b		0.92	0.69	−0.88	−1.19	−1.72	−2.12	
10c	0.92	0.51	0.27	−0.79	−1.10	−1.31	−1.71	−2.12

[a] Values are in Volts relative to a ferrocene/ferrocenium couple and obtained by DPV. Conditions: 0.1 M $(n\text{-}Bu)_4NPF_6$ in 1,2-dichlorobenzene, the working electrode and counter electrode are Pt wire, the reference electrode is Ag/0.01 M $AgNO_3$ and 0.1 M $(n\text{-}Bu)_4NClO_4$ in CH_3CN. Pulse width, 50 ms; pulse period, 200 ms; scan rate, 20 mV s^{-1}.

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