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Regiocontrolled Synthesis of 1,2-Di(organo)fullerenes via Copper-Assisted 1,4-Aryl Migration from Silicon to Carbon

Ying Zhang, Yutaka Matsuo,* and Eiichi Nakamura*

Department of Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku,
Tokyo 113-0033, Japan

matsuo@chem.s.u-tokyo.ac.jp; nakamura@chem.s.u-tokyo.ac.jp

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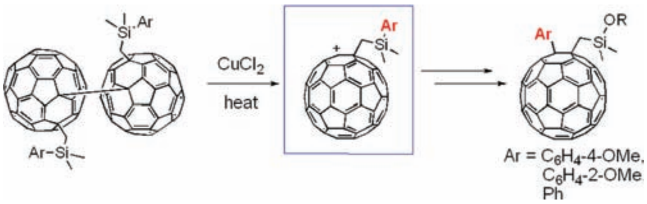
ABSTRACT



A concise and efficient way to generate fullerene cationic species through the oxidation of a fullerene radical or a fullerene anion with a Cu(II) salt has been developed. It was demonstrated that the cationic fullerene is useful for functionalization of fullerene, in particular, for the synthesis of noncyclic 1,2-di(organo)[60]fullerene derivatives that can be selectively prepared through intramolecular 1,4-aryl migration of an aryl group from a silicon atom to the fullerene core.

Regioselectivity is a central issue in organic synthesis and so is important in fullerene functionalization.[1,2] Introduction of two organic addends to [60]fullerene, for instance, the addition of R and R′ groups across a double bond, can yield 1,2- and 1,4-addition products (Scheme 1a). In fullerene chemistry, the former has been found to occur only in the addition of sterically small cyano[3] and methyl groups[4] (or hydrogen atoms), while the 1,4-adduct is always a major or exclusive product in the addition of bulkier groups.[5−8] The putative pentadienyl radical, cationic, or anionic intermediate (marked with red color in Scheme 1a) preferentially produces the 1,4-adduct because of either the inherent nature of the pentadienyl species to react on the central carbon or steric hindrance due to the R group or both. Here, we report a new method to control this regioselectivity by exploiting the ability of an arylsilane to act as an intramolecular donor of an aryl group to the carbocationic species (Scheme 1b). This method provides a synthetic entry to 1,2-di(organo)-[60]fullerenes that have so far been unavailable except for cycloaddition products (e.g., C61-butyric acid methyl ester (PCBM) widely used for photovoltaic research).[9]

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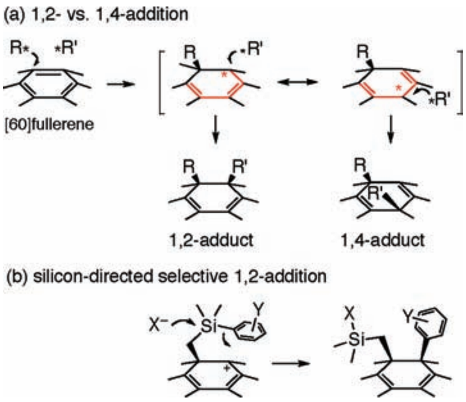
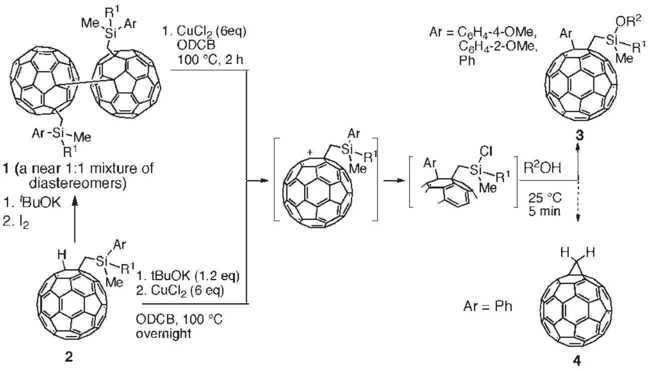
10.1021/ol202511u

Scheme 1. 1,2- vs 1,4-Addition via a Pentadienyl Species and Silicon-Directed Regioselection



We discovered this reaction during the screening of substrates on the $CuCl_2$-mediated synthesis of methanofullerene[10] from an arylsilylmethylfullerene dimer **1**, which was synthesized very cleanly in quantitative yield by treatment of the corresponding silylmethylfullerene **2** with a base and an oxidant as described previously.[10] The silylmethylfullerene **2** is available in good yield by addition of a Grignard reagent to [60]fullerene in the presence of *N*,*N*-dimethylformamide.[6] Note that **1** formed as a nearly 1:1 mixture of diastereomers, which equilibrate with each other upon heating at 100 °C via a fullerene radical.[11,12]

Scheme 2. $CuCl_2$-Mediated Conversion of Silylmethylfullerenes **1** and **2** to Arylfullerene **3** and Methanofullerene **4**



When the (phenyldimethyl)silylmethylfullerene dimer **1a** was treated with 6 equiv of $CuCl_2$ at 100 °C in *o*-dichlorobenzene (ODCB) and then with MeOH, we obtained a phenylated compound **3a** in addition to the methanofullerene **4** (Scheme 2, Table 1). Increasing the number of phenyl groups on the silicon atom (**1b**) resulted in a higher yield of the phenylated compound **3b**. Using more electron-rich aryl groups (**1c** and **1d**) resulted in exclusive formation of the arylated products in high yield.

Inorganic Cu(II) salts, CuX_2 (X = Cl, Br, OTf) are equally effective,[13] while inorganic Cu(I), Fe(III), and Mn(III) salts were entirely ineffective. The use of 6 equiv (3 equiv/fullerene) was necessary to achieve full conversion of the starting material (a double amount of copper is necessary while using fullerene monomer **2**). The reaction can be conducted under either nitrogen or air.[14]

These results suggest a mechanism that a cationic fullerene intermediate[7] was generated by oxidation of a fullerene radical with $CuCl_2$, and that the intermediate reacted with the Si−Ph bond to produce **3**, and with the Si−CH_2 bond to produce **4**.

Table 1. Copper-Mediated Synthesis of 1,2-Di(organo)fullerene **3** from Fullerene Dimer **1**^{a}

entry	substrate	Ar	R^1	**3**^{a} (%)	**4**^{a} (%)
1	**1a**	Ph	Me	49 (**3a**)	46
2	**1b**	Ph	Ph	67 (**3b**)	26
3	**1c**	C_6H_4-4-OMe	Me	90 (**3c**)	
4	**1d**	C_6H_4-2-OMe	Me	92 (**3d**)	

^{a} See Scheme 2 and the Supporting Information for conditions.

We started with the arylsilylmethyl[60]fullerene **2** by removal of the proton attached to the fullerene core with *t*-BuOK followed by oxidation of the anion with $CuCl_2$ and treatment with MeOH (Table 2). The reaction took place in the same manner as the one starting with a dimer (entries 1−5), while the overall yield of the products was lower in this one-step synthesis because of some complications in the first oxidation step. Quenching the reaction with water afforded a silanol, which was difficult to purify because of siloxane formation (entry 6),[15] and quenching with *i*-PrOH gave a stable isopropoxysilane compound **3g**. In this manner, the substituents of the 1,2-di(organo) fullerene adducts could be easily modified, which is beneficial for their applications in organic electronics devices.

Table 2. Copper-Mediated Synthesis of 1,2-Di(organo)fullerene **3** from Arylsilylmethylfullerene **2**^{a}

entry	substrate	Ar	R^1	R^{2b}	**3**^{a} (%)	**4**^{a} (%)
1	**2a**	Ph	Me	Me	38 (**3a**)	52
2	**2b**	Ph	Ph	Me	46 (**3b**)	34
3	**2c**	4-$MeOC_6H_4$	Me	Me	66 (**3c**)	trace
4	**2d**	2-$MeOC_6H_4$	Me	Me	78 (**3d**)	trace
5	**2e**	2-$^iPrOC_6H_4$	Me	Me	67 (**3e**)	trace
6	**2d**	2-$MeOC_6H_4$	Me	H^c	81 (**3f**)	trace
7	**2d**	2-$MeOC_6H_4$	Me	^{i}Pr	66 (**3g**)	trace

^{a} Isolated yield. ^{b} Anhydrous alcohol was used. ^{c} Water was used to quench the reaction.

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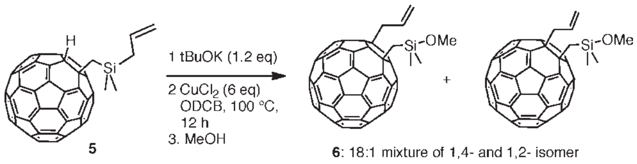
The reaction of an allyldimethylsilylmethylfullerene **5** under the same conditions afforded an 18:1 mixture of 1,4- and 1,2-compounds **6** (Scheme 3). We speculate that the reaction initially gave a 1,2-adduct, which subsequently underwent a Cope rearrangement during heating. Brief attempts to probe the mechanism using a crotyl group were hampered by the formation of a regioisomeric mixture of the crotylsilane starting material.

Scheme 3



With possible applications to organophotovoltaic research in mind,[6,16] we obtained electrochemical data for these compounds and compared them with those of PCBM. The cyclic voltammetry measurement was thus performed to elucidate the electrochemical properties of the 1,2-diadducts **3a**−**e**,**g** as well as the 1,4-diadduct **6** (the 1,4-isomer of **6**) (Table 3). For all compounds, the voltammograms exhibited three reversible waves on reduction. The first reduction potentials for all compounds were more negative than those for PCBM. The aryl group being directly attached to a fullerene core, we expected that the LUMO level of fullerenes **3** could be controlled more readily than in the case of PCBM derivatives where the phenyl group is attached to the methano bridge on the fullerene core.

We noted that the compounds **3d**, **3e**, and **3g** bearing an electron-donating alkoxyl group on the phenyl ring at the 2-position showed a higher LUMO level, −3.73 eV, than those where it was at the 4-position (**3c**), suggesting that the 2-methoxy group donates electrons much more readily than the 4-methoxy group—a rather unconventional observation in the context of standard organic chemistry. In addition, **3d** bearing a methyldiphenylsilylmethyl group also has a LUMO level of −3.73 eV as distinct from **3a** bearing a dimethylsilylmethyl group, indicating a significant effect of the difference of one remote phenyl group. This is also anomalous.

Table 3. Reduction Potentials of Di(organo)[60]fullerenes Compared with Those of PCBM[a]

compd	$E_{1/2}^{\mathrm{red1}}$/V	$E_{1/2}^{\mathrm{red2}}$/V	$E_{1/2}^{\mathrm{red3}}$/V	LUMO level/eV
PCBM	−1.00	−1.59	−2.19	−3.80
3a	−1.03	−1.59	−2.21	−3.77
3b	−1.07	−1.65	−2.28	−3.73
3c	−1.02	−1.59	−2.22	−3.78
3d	−1.01	−1.57	−2.20	−3.79
3e	−1.07	−1.65	−2.28	−3.73
3g	−1.07	−1.64	−2.27	−3.73
6[c]	−1.03	−1.60	−2.20	−3.77

[a] Potential in volts vs a ferrocene/ferrocenium couple was measured by cyclic voltammetry in THF solution containing $Bu_4N^+PF_6^-$ (0.1 M) as a supporting electrolyte at 25 °C with a scan rate of 0.05 V/s. Glassy carbon, platinum wire, and Ag/Ag$^+$ electrodes were used as working, counter, and reference electrodes, respectively. [b] The values for the LUMO level were estimated using the following equation: LUMO level = $-(4.8 + E_{1/2}^{\mathrm{red1}})$ eV. See ref 17. [c] The data is for the 1,4-isomer. The two isomers can be isolated.

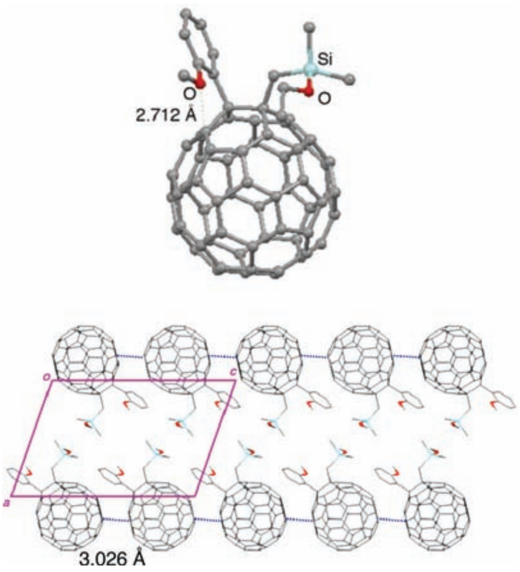


Figure 1. (a) Crystal structure of $C_{60}(CH_2SiMe_2OEt)(C_6H_4\text{-}2\text{-}OMe)$. (b) Crystal packing of $C_{60}(CH_2SiMe_2OEt)(C_6H_4\text{-}2\text{-}OMe)$ along the *b* axis.

We obtained a black crystal of $C_{60}(CH_2SiMe_2OEt)$-$(C_6H_4\text{-}2\text{-}OMe)$ (an ethoxysilane instead of the isopropoxy compound **3g**) suitable for crystallographic analysis (Figure 1) and gained insight into a possible reason for the anomalously raised LUMO level for the 2-methoxy compounds (i.e., compound **3e**). The crystal structure showed a close packing of fullerene molecules without solvent molecules. The distance between the oxygen atom of the 2-methoxy group on the phenyl ring and the nearest carbon atom on the fullerene core was found to be 2.712 Å, and the oxygen lone pair was apparently pointing toward the surface of the fullerene π-system.

An interesting feature is the fullerene−fullerene distance of 3.026 Å (for the nearest neighboring carbon atoms), which is much shorter than the distance of 3.186 Å found for

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(13) The conversion is the same, but the ratio of **3** and **4** is different.

(14) This is true only when a dimer is used.

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a structurally related bis(dimethylphenylsilylmethyl)[60]-fullerene (SIMEF).[6] This feature is potentially beneficial for n-type semiconductors[18,19] and is to be examined in depth in the future.

In summary, we have achieved the selective synthesis of 1,2-di(organo)fullerenes, which have so far been difficult to obtain. This new method allows us to synthesize these compounds in two to three steps from [60]fullerene in 40−75% overall yields. The experimental observations suggest that the present reaction as well as the cyclopropanation that we reported recently[10] take place via a cationic fullerene intermediate generated either from a dimer or from a fullerene anion by oxidation with Cu(II).

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Supporting Information Available. Synthetic procedures for and characterization of 1,2-di(organo)fullerene derivatives, X-ray crystal structure, and their electrochemical properties. This material is available free of charge via the Internet at http://pubs.acs.org.

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