Walk on the Sphere: Electrochemically Induced Isomerization of C_{60} Bis-adducts by Migration of Di(alkoxycarbonyl)methano Bridges

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Cyclopropanation with malonate esters (Bingel reaction)[1] has been widely used for the preparation of mono- and polyadducts of C_{60}[2] and the higher fullerenes.[3] The cyclopropane rings fused to the carbon spheres have generally been found to be highly stable. Only the monoanion of 1,2-methano[60]fullerene-61,61-dinitrile was reported by Wudl and co-workers[4] to revert back to C_{60}, as evidenced by cyclic voltammetry (CV). Also, some of us had noted that bis(methano)fullerenes with a *cis*-2-addition pattern exhibit a chemically irreversible second one-electron reduction, using CV and steady-state voltammetry (SSV) on a rotating disk electrode.[5] Recently, our research group discovered that exhaustive controlled potential electrolysis (CPE) of diethyl 1,2-methano[60]fullerene-61,61-dicarboxylate leads to the removal of the cyclopropane rings from the carbon sphere to yield predominantly C_{60}.[6] This conversion was called the retro-Bingel reaction and has been successfully employed to remove up to four di(alkoxycarbonyl)methano groups from a variety of covalent adducts of C_{60}, C_{70}, C_{76}, as well as C_{2v}- and D_3-C_{78}.[6,7] Here, we report the unexpected electrochemically induced isomerization of fullerene adducts by migration of the cyclopropane rings on the C_{60} surface, if the CPE is not exhaustive. This unprecedented electrochemical *walk on the sphere* rearrangement has been observed for the six regioisomeric bis-malonate adducts **1**−**6**[2c,5,8] (Figure 1). Only a few examples of chemical rearrangements of addends on the fullerene surface have been reported previously.[9−15]

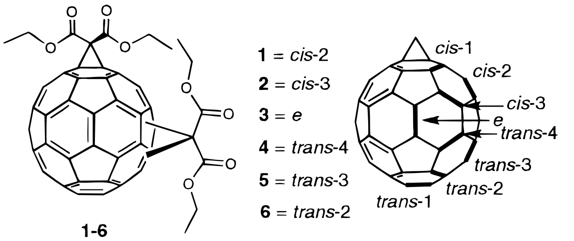

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Figure 1. Representation of the C_{60} bis-adducts **1**−**6** which were subjected to CPE at the first and second reduction potential.

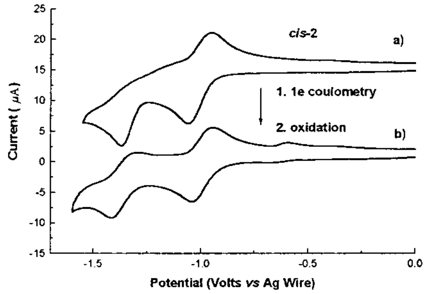

Figure 2. (a) CV of *cis*-2-bis-adduct **1** in CH_2Cl_2 (+0.1 M Bu_4NPF_6) using a scan rate of 100 mV s^{-1}. (b) Voltammogram recorded after coulometrically controlled one electron per molecule electrolysis, followed by reoxidation, clearly showing that the second reduction has become more chemically reversible. The working electrode was a glassy carbon mini-electrode.

The *cis*-2-bis-adduct **1** was subjected to CPE to its monoanionic state (at −1.2 V versus a Ag wire pseudo-reference electrode separated from the solution using a Vycor tip). The charge transferred corresponded exactly to one electron per molecule. Changes in the CV indicated that a chemical transformation had occurred since the second reduction, initially chemically irreversible, became more reversible (Figure 2). After 30 min in its monoanionic state, reoxidation of the solution at 0 V (vs Ag, 80% of charge recovered), followed by column chromatography (SiO_2, CH_2Cl_2/hexane 3:1), yielded a mixture of bis-adducts (44%), which was analyzed by HPLC.[16] The analytical chromatogram showed that the *cis*-2 isomer had completely disappeared and the *e*-bis-adduct had become the predominant component in the newly formed product mixture (*e*, 57%; *trans*-3, 31%; *trans*-4, 8%;

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(16) Analytical HPLC was performed on a Macherey-Nagel AG Nucleosil 100−7 (7 μm) 250 mm × 4 mm column using a toluene mobile phase at a flow rate of 2 mL/min. The percentages of the individual bis-adducts in the mixture were determined from integrated HPLC peak areas with optical detection at $\lambda = 310$ nm and corrected for the difference in UV−vis absorption at this wavelength.

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Table 1. Relative Distribution[a] of C_{60} Bis-adducts after Coulometric Two-Electron CPE

starting material	*cis*-(1−3)	*e* (**3**)	*trans*-4 (**4**)	*trans*-3 (**5**)	*trans*-2 (**6**)	*trans*-1	mono[b]	yield[c]
cis-2 (**1**)		23%	5%	8%	52%	12%	29%	49%
cis-3 (**2**)		22%	6%	10%	51%	11%	28%	53%
e (**3**)		26%	9%	12%	44%	9%	10%	44%
trans- 4 (**4**)		23%	10%	12%	47%	8%	14%	61%
trans- 3 (**5**)		23%	9%	12%	46%	10%	23%	43%
trans- 2 (**6**)		22%	6%	9%	53%	10%	19%	39%
$[(PrOOC)_2C]_2C_{60}$		25%	8%	12%	46%	9%	24%	55%

[a] The relative percentages of bis-adducts were determined from the integrated HPLC peak areas. [b] Absolute isolated yield of diethyl 1,2-methano[60]fullerene-61,61-dicarboxylate. [c] Absolute recovered yield of bis-adducts.

cis-3, 4%). The isomeric bis-adducts **2**−**5** were submitted to the same protocol (CPE to convert them to their corresponding monoanions); however, no isomerization was observed and only the starting materials were recovered in yields ranging from 75 to 90%.

These unexpected results led us to investigate the behavior of the six regioisomers **1**−**6** upon coulometrically controlled two electron per molecule electrolysis. The CPE at the second reduction potential (around −1.55 V vs Ag) of each individual isomer was stopped after coulometrically determining that two electrons per molecule had been transferred. In some cases, changes in the CV clearly indicated that an irreversible chemical transformation had taken place. Coulometric reoxidation of the solution at 0 V (vs Ag, 60−70% charge recovered), followed by column chromatography as described above, yielded two fractions, one containing diethyl 1,2-methano[60]fullerene-61,61-dicarboxylate from loss of one methano addend by the retro-Bingel reaction[6] and the other one a mixture of regioisomeric bis-adducts. To our surprise, HPLC analysis showed practically identical relative product distributions for the isolated mixtures of bis-adducts, regardless of which isomer was electrolyzed (Table 1). Thus, malonate bridges appear to be migrating around the fullerene sphere, but not in a random manner. The product mixtures obtained by electrolysis of the six bis-adducts **1**−**6** did not contain any of the *cis*-2- and *cis*-3-adducts. These derivatives, with two cyclopropane rings located in close proximity in one hemisphere, had been calculated to be the most strained of the isolable regioisomeric bis(methano) adducts.[2b,8a] Strain release may thus provide some of the driving force for the quantitative isomerization of the *cis*-2- and *cis*-3-bis-adducts **1** and **2**, respectively, and correspondingly, these compounds are not formed during CPE of the other regioisomers. The major isomer being formed is always the *trans*-2-derivative (40−50%). It is important to point out that ∼10% of the *trans*-1-bis-adduct is produced in every case and that the *trans*-1- and *trans*-2-isomers, therefore, appear roughly in their expected 1:4 statistical ratio. This result is especially noteworthy since when diethyl 1,2-methano[60]fullerene-61,61-dicarboxylate undergoes a Bingel reaction with 1 equiv of diethyl 2-bromomalonate, only 0.8−2% of *trans*-1-regioisomer can be isolated.[8a,b] The *trans*-1- and *trans*-2-(**6**) derivatives predominate over the *trans*-3 (**5**) and *trans*-4 (**4**) ones, while the *e*-isomer (**3**) is also formed in high percentage (∼25%). The preferred formation of both *e*- and *trans*-isomers could be a consequence of their inherently higher stability, as compared to the *cis*-derivatives, which had been predicted by theoretical calculations.[8a] The fact that the same product distribution is observed after coulometric reduction of the compounds (**1**−**6**) with two electrons suggests that the isomerization occurs under thermodynamic control.

The mechanism of this novel isomerization is now under investigation. As a working hypothesis, we propose that, after introduction of two electrons into an isomer, a bond to one of the cyclopropane rings is broken, thus giving rise to a singly bound stabilized malonate anion[17] which might undergo "*moonwalking*" around the carbon sphere which presumably delocalizes the second electron. The migration could occur one foot at a time, involving sequential formation and breaking of methano bridges at 6−5 and 6−6 junctions, until the thermodynamic equilibrium of the dianionic species is reached. A thermal barrier should exist for such migrative steps and, in agreement with this expectation, the rearrangement is completely inhibited if CPE is performed at −78 °C.

Proof that the isomerization occurs intra- and not intermolecularly was obtained from the $2e^-$ CPE of a solution containing a 1:1 ratio of the mixture of seven bis[(diethoxycarbonyl)methano] adducts $\{[(EtOOC)_2C]C_{60}\}$ and the mixture of the corresponding seven bis[(dipropoxycarbonyl)methano] adducts $\{[(PrOOC)_2C]$-$C_{60}\}$ that are obtained by Bingel reaction of C_{60} with 2 equiv of diethyl and dipropyl malonate, respectively.[8a] No mixed adducts, or only traces, containing both $(EtOOC)_2C$ and $(PrOOC)_2C$ addends were detected after reoxidation, by either HPLC or MALDI-TOF-MS, within experimental error. The HPLC depicted only two sets of peaks, one set for the products formed by intramolecular shuffling of the $(EtOOC)_2C$ addends and another one for the products formed by intramolecular migration of the $(PrOOC)_2C$ addends. The relative product distribution in each of the two sets of compounds was identical to the one given in Table 1. As additional proof of the intramolecularity of the rearrangement, tris-adducts were never detected. We now intend to optimize the experimental setup in such a manner that the isomerization procedure can be used to produce larger amounts of bis-adducts such as *trans*-1 and *trans*-2, which are not readily available by other methods.[18]

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Supporting Information Available: Description of the electrochemical setup and experiments, typical HPLC of *e*-bis-adduct **3** after $2e^-$ CPE, MALDI-TOF-MS and HPLC as proof of the intramolecularity of the isomerization, and experimental description of the preparation of $[(PrOOC)_2C]_2C_{60}$ and $[(PrOOC)_2C][EtOOC)_2C]C_{60}$ (mixtures of regioisomers) (6 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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