

Reductive Electrochemistry of Spiromethanofullerenes

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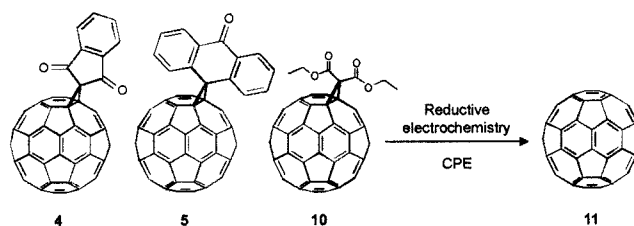
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The synthesis and electrochemical properties of spiro-methanofullerenes **1–6** are described. The syntheses were achieved via the diazomethane route, and the regioisomeric distribution of bis-adducts **3** was determined by ¹H NMR, UV–vis, and HPLC analysis. The electrochemistry of these compounds in dichloromethane exhibits, besides several reversible reductions, some irreversible waves. Reductive electrolysis of **1** and **3–5** in dichloromethane leads to the removal of the addend and thus to the formation of C₆₀. Reductive electrolysis of **1**, **2** and **6** in dichloromethane leads to a different reaction, which we tentatively assign to a reaction with the solvent to form fullerene–CH₂Cl products. Electrolyses in the less reactive solvent THF lead to adduct removal for **1** and **3–5**. Interestingly, significant formation of bis-adducts from the corresponding monoadducts was observed for **4** and **5**. These electrochemically induced reactions, namely addend removal, reaction with the solvent, and addend transfer are influenced by the structure of the addend and by the choice of solvent.

Introduction

The Bingel reaction, cyclopropanation of fullerenes by the addition of malonate derivatives, has been widely used as a synthetic tool for the preparation of fullerene adducts.¹ Its reverse, the electrochemical retro-Bingel reaction, was recently reported by Diederich and Echegoyen (see Scheme 1, **10** to **11**).² The reaction, an electrolytic reduction reaction typically performed in dichloromethane, efficiently removes di[alkoxycarbonyl]-methano adducts to yield the parent fullerenes. Interestingly, partial electrolysis of bis- or tris-Bingel adducts of C₆₀ results in isomerization of the adducts.³ The “Bingel-[retro-Bingel]” strategy can be used as a protection–deprotection scheme and has been used for the isolation of enantiomerically pure C₇₆^{2a} for the preparation of a new C_{2v}-C₇₈ bis-adduct^{2b} and in the separation of constitutional isomers and enantiomers of C₈₄.^{2c} Bingel addends can also be removed chemically using Mg/Hg in THF at elevated temperatures,⁴ and both the electrochemical and chemical procedures have been shown to act selectively in the presence of several other adduct types.^{4,5}

Scheme 1. Adduct Removal by Reductive Electrochemistry for Methanofullerenes **4**, **5**, and **10**



We have also shown that addend removal via electrolytic reduction is not limited to Bingel-type adducts (see fullerene **10**), but can also occur for spiro-methano adducts such as those on **4** and **5** (see Scheme 1). We showed that controlled potential electrolysis (CPE) in dichloromethane results in the efficient removal of these adducts, to form the parent C₆₀.⁶ Adduct removal for these methanofullerenes during electrolysis is presumably initiated by opening of the three-membered ring.⁷ Furthermore, reductive electrochemistry of **4** and **5** in THF revealed, besides simple adduct removal, a second reaction pathway leading to the formation of bis-adducts.⁸

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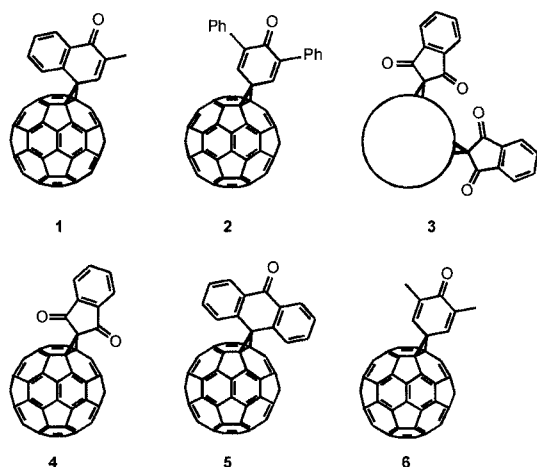
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Chart 1. Spiromethanofullerenes 1-6 Studied by Reductive Electrochemistry

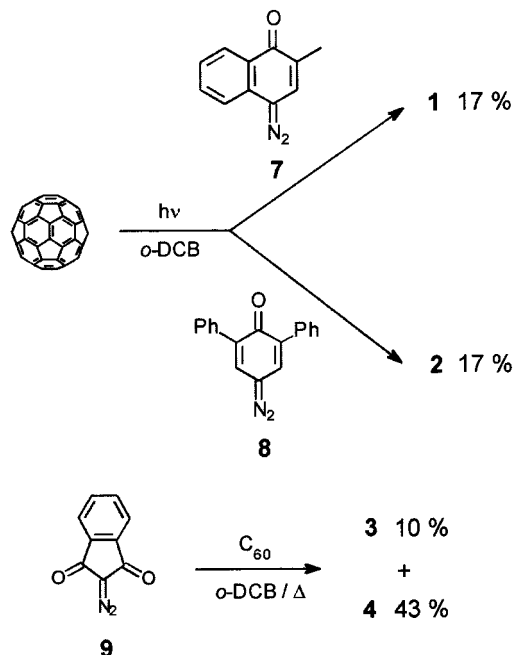
While some aspects of the electrochemical transformations of a few of these molecules have been discussed in preliminary reports,^{6,8} here we report the synthesis of some new methanofullerene derivatives (Chart 1), along with the assignment of the regioisomers of bis-adducts **3** by detailed analysis using UV-vis, ¹H NMR, and HPLC. The products resulting from the reductive electrochemistry of **1-6** in the solvents dichloromethane and THF are also described for the first time along with an overall picture of the electrochemistry of this class of molecules. A previously unreported electrochemically induced reaction is also presented, for which we tentatively propose involvement of the solvent dichloromethane.

Results and Discussion

Synthesis and Characterization of the Methanofullerenes. The synthesis and electrochemical properties of **4-6** in dichloromethane were described previously.^{6,7,9} Compounds **1-3** have somewhat similar structures but were designed to probe the effects of the different groups on the electrochemical reactions. Thus, **1** is a structural hybrid between **5** and **6**, while **2** contains phenyl groups on the quinone instead of the methyl groups in **6**. Compound **3** is the regioisomeric mixture of bis-adducts corresponding to the monoadduct **4**.

The synthesis of the spiromethanofullerenes **1-4** was carried out by reaction of C₆₀ with the respective diazo compounds **7-9** by irradiation with a sun lamp (**7** and **8**) or by heating in 1,2-dichlorobenzene (*o*-DCB) (**9**) under a nitrogen atmosphere (see the Experimental Section) (Scheme 2).

The starting diazo compounds **7**¹⁰ and **8**¹¹ were prepared by Bamford-Stevens reaction from the respective *p*-benzoquinone derivatives and *p*-tosylhydrazone under basic conditions. Diazo compound **9** was prepared from commercially available indandione by reaction with *p*-

Scheme 2. Synthesis of Novel Spiromethanofullerenes from Diazo Compounds

tosyl azide following the method previously reported in the literature.¹²

As shown in Scheme 2, monoadduct **4** (43% yield, 62% based on recovered C₆₀) was obtained together with a mixture of regioisomeric bis-adducts (**3**) in lower yield (10%, 13% based on recovered C₆₀).

All the obtained spiromethanofullerenes **1-6** were the thermodynamically more stable [6,6] closed methanofullerene isomer showing the typical absorption peak at around 430 nm in the UV-vis spectra. The ¹³C NMR spectra of the spiromethanofullerenes show, in addition to the carbonyl groups at 184–191 ppm, the presence of the cyclopropane carbons in the region between 40 and 77 ppm for **1, 2, 4, and 5**. The FTIR and FABMS spectra are also consistent with the assigned structures.

It is worth mentioning that the ¹H NMR spectra show a remarkable downfield shift of the protons nearest to the C₆₀ surface for compounds **1, 2, 5, and 6** in comparison to those of the parent diazo starting materials as it has been previously observed for other compounds^{7d,13} due to the magnetic deshielding effect of the ring currents of the C₆₀ sphere.

Bis-adducts of [6,6]methanofullerenes can consist of eight possible regioisomers: *trans*-1–4, *e*, and *cis*-1–3. Unambiguous assignment of regioisomers of several fullerene bis-adducts has been described in detail by Hirsch et al.¹⁴ For example, synthesis of bis-Bingel adducts of C₆₀ leads to the following regioisomer distribution: 2% *trans*-1, 13% *trans*-2, 30% *trans*-3, 9% *trans*-4, 38% *e*, 6% *cis*-3, and 2% *cis*-2.¹⁴ The regioisomer distribution that results during the synthesis of the bis-adducts

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(9) Methanofullerene **6** is unstable under reductive conditions. Products obtained after electrolysis of methanofullerene **6** do not contain any C₆₀ or starting material. Main peak in Maldi-Tof is at *m/z* 890.

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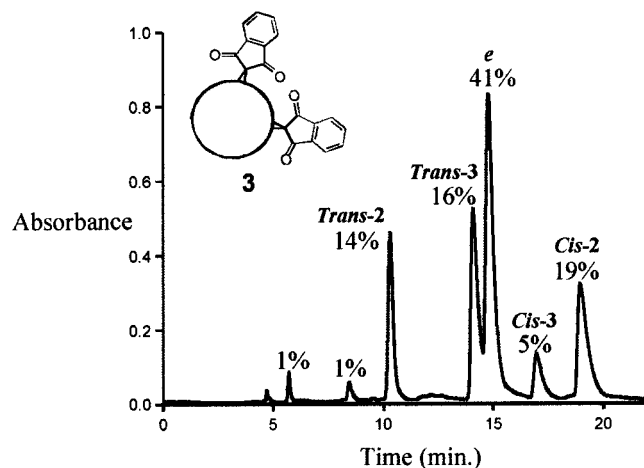


Figure 1. HPLC graph of the regioisomers of bis-adduct **3**.

3 can be studied by HPLC, and the chromatogram is shown in Figure 1. We separated the regioisomeric bis-adducts **3** on a preparative HPLC column (eluent: toluene; column: Supelco SPLC-Si silica semipreparative column). Five fractions were isolated and their structures were assigned by ^1H NMR spectroscopy (Figure 2), UV-vis spectroscopy (Figure 3), and using polarity arguments. The signals in the ^1H NMR spectrum of the monoadduct **4** are typical of an AA'XX' spin-system, as expected for an ortho-substituted benzene derivative; see Figure 2.¹⁵ The ^1H NMR spectra for the isolated regioisomers of **3** (spin-system AA'BB'XX'YY') are generally quite complex (Figure 2), but symmetry arguments enabled the unambiguous assignment of the third fraction as that corresponding to the *e* isomer. This is the case because it has C_s symmetry and it is the only regioisomer with one adduct in the plane of symmetry. This results in a more complicated ^1H NMR spectrum compared to the other regioisomers, as visualized by the distribution of the peaks. The ^1H NMR spectrum of the *e* regioisomer consists of two sets of two peaks with the following number of protons: 2H/3H and 1H/2H, whereas the other ^1H NMR spectra consist of two sets of peaks with a 4H and 2H/2H distribution.¹⁶ The other isomer that could have been immediately assigned if it had been isolated would have been the highly symmetric *trans*-1 (with D_{2h} -symmetry), but this was not observed. The other isomers were assigned by UV-vis spectroscopy and by their polarity, as reflected in the order of elution on the HPLC column. It was assumed that the HPLC elution order would follow the polarity of the regioisomers (increasing polarity from *trans*-1 to *cis*-1), as observed by Hirsch for the Bingel bis-adducts.¹⁴ Assignment of the second fraction to the *trans*-3 regioisomer (and not *trans*-4) was based on the UV-vis spectrum. The following regioisomer distribution of the bis-adducts was found for the diazomethane synthetic product mixture: 14% *trans*-2, 16% *trans*-3, 41% *e*, 5% *cis*-3, 19% *cis*-2 (Figure 1). No detectable amount of the *trans*-4 regioisomer was isolated, perhaps because it elutes very close to the *e* or the *trans*-3 isomers. The distribution is similar to that of the bis-Bingel addend fullerenes determined by Hirsch et

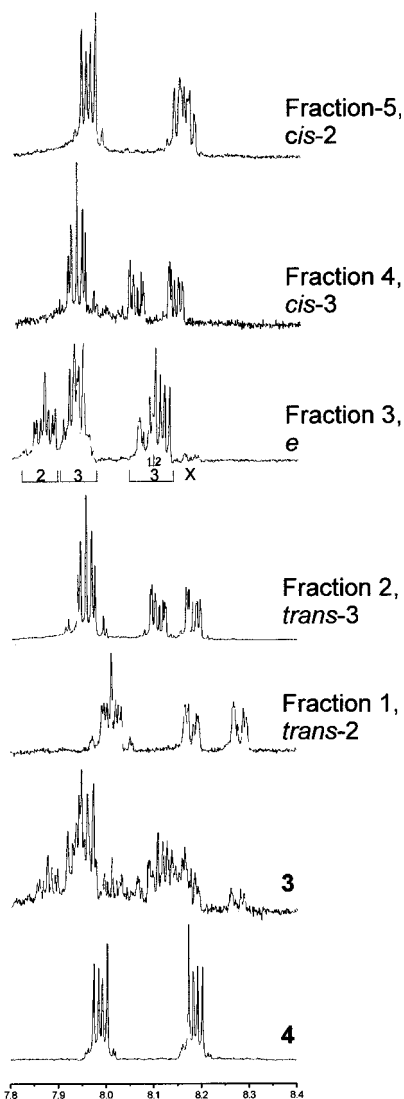


Figure 2. ^1H NMR spectra of the regioisomers of bis-adduct **3** (HPLC fractions 1–5), bis-adduct **3**, and monoadduct **4**.

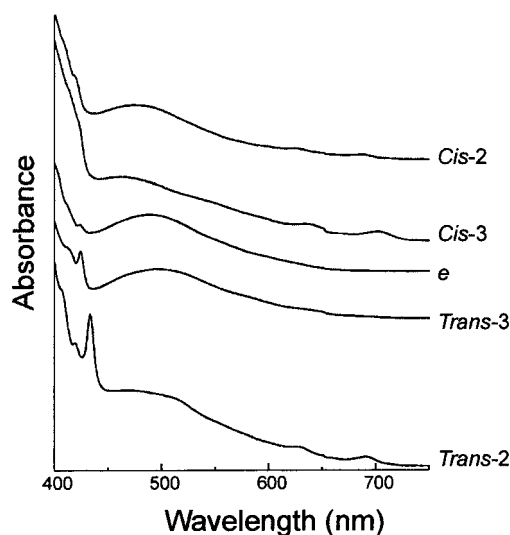


Figure 3. UV-vis spectra of the regioisomers of bis-adduct **3**.

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(16) Fraction 3 (*e* isomer) contains a small amount (7%) of the *trans*-3 isomer, causing the NMR-signal denoted with X.

al.,¹⁴ with *trans*-3 and *e* as predominant regioisomers and *cis*-3 as one of the minor ones.

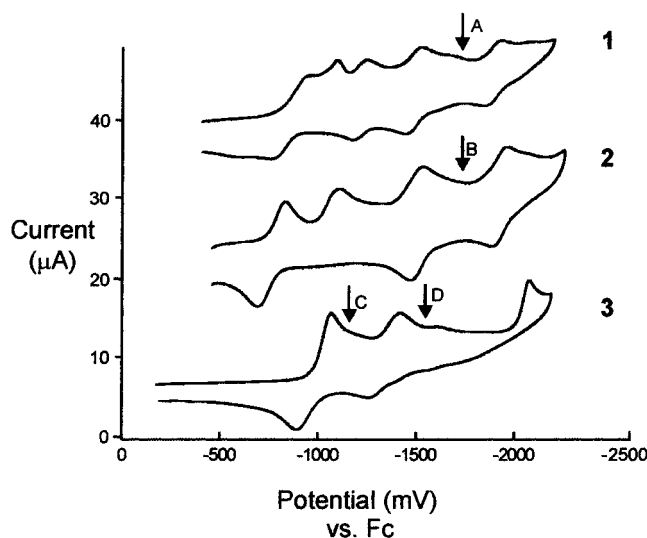


Figure 4. Cyclic voltammograms vs ferrocene of **1–3** in dichloromethane.

Table 1. Redox Potentials of Methanofullerenes **1–6 vs Ferrocene in Dichloromethane**

| | E_1 | E_2 | E_3 | E_4 | E_5 |
|----------|-------------------|--------------------|--------------------|-------|-------|
| 1 | -951 ^a | -1096 ^b | -1207 | -1486 | -1841 |
| 2 | -832 ^c | -1092 ^d | -1487 | -1915 | |
| 3 | -965 ^e | -1335 | -2069 ^c | | |
| 4 | -971 ^e | -1598 | -2015 | | |
| 5 | -1038 | -1383 ^c | -1492 | -1893 | |
| 6 | -859 | -1119 ^c | -1522 | -1926 | |

^a Electrochemically irreversible reduction, oxidation wave at -595 mV. ^b Electrochemically irreversible reduction, oxidation wave at -724 mV. ^c Electrochemically irreversible reduction. ^d Electrochemically irreversible reduction, oxidation wave at -666 mV. ^e Two-electron process.

Electrochemistry in Dichloromethane. The cyclic voltammograms (CVs) of **1–3** in dichloromethane are presented in Figure 4. Compound **1** exhibits two chemically irreversible redox waves, followed by three reversible ones. The CV of **2** consists of two irreversible redox waves followed by two reversible waves. Compound **3** starts with a two-electron wave, followed by a one-electron wave and an irreversible wave. Similar to the electrochemistry of **4–6**,⁶ **1–3** exhibit, besides reversible reductions, several irreversible reductions. The redox potentials of **1–6** vs ferrocene are reported in Table 1.

Compound **1** was subjected to controlled potential electrolysis (CPE) after the fourth reduction wave (arrow A, Figure 4), which discharged 3.4 electrons per molecule. The CV of **1** completely changed upon electrolysis. After reoxidation at 0 V, the reaction mixture was purified by column chromatography (eluent: toluene) to yield 38% of fullerene-based products. Characterization by HPLC, UV-vis spectroscopy, and Maldi-Tof mass spectrometry showed that no starting material was recovered while two products, in a roughly 1:1 ratio, were isolated. One of the products was identified as C₆₀, and the other was an unknown product with a mass of 926 amu (**1**: 876 amu). So adduct removal is one of the main reaction pathways for **1**, but a secondary pathway affords a new, still uncharacterized product. Interestingly, the electrolysis of **6** under identical conditions resulted in the formation of a product whose mass is also 50 amu larger than that of the starting material (**6**, 840 amu; electrolysis product, 890 amu).⁶ However, in the case of **6**, no C₆₀ was

isolated after the electrolysis. We recently showed that dichloromethane reacts efficiently with the [60]fullerene trianion to form methanofullerenes of the type C₆₀>(CH₂)_n,¹⁷ and it also forms similar adducts with C₈₄ (C₈₄>(CH₂)_n) during the reductive retro-Bingel reaction of di[alkoxycarbonyl]methano adducts of C₈₄.^{2c} We think that a similar process is taking place during the electrolysis of **1** and **6**. These anions can react with dichloromethane to form products of the type methanofullerene-CH₂Cl, which presumably acquires another proton during or after oxidation, leading to the observed mass increase of 50 amu. Due to the small amounts of material available, it has not been possible to carry out an assignment (e.g., by ¹H NMR) of the structures of these +50 amu products.¹⁸

CPE of **2** (964 amu) was performed after the third wave (arrow B, Figure 4) discharging 3.2 electrons. Reoxidation and purification yielded two fullerene products in a 1:1 ratio with a total 58% yield. Some starting material was isolated indicating that this compound is relatively stable under reductive electrolysis conditions. Furthermore an unknown product with a mass of 1014 amu was isolated, which again is assigned to a reaction product with dichloromethane, leading to **2-CH₂Cl**.

Electrolysis of **4** after the first reduction wave resulted in the formation of C₆₀ in a relatively high yield (58%).⁶ We performed several electrolysis experiments with the corresponding bis-adducts **3**. CPE of **3** at a potential slightly cathodic of the second wave (arrow D, Figure 4) discharged 3.4 electrons and yielded 75% of fullerene products.¹⁹ Purification and analysis showed the exclusive formation of C₆₀. Isomers **3** also exhibit adduct removal induced by reductive electrochemistry. Electrolysis at less negative potentials, e.g., after the first two-electron wave (arrow C, Figure 4), discharged 2.5 electrons and yielded 70% of fullerene products. Purification and analysis showed the formation of C₆₀ (35%) and monoadduct **4** (35%). We observed that this electrochemical adduct removal reaction is a relatively slow reaction and can be inhibited considerably if the electrolysis mixture is immediately reoxidized after completing the reductive electrolysis.²⁰ CPE after the first oxidation wave (arrow C, Figure 4) yielded 30% monoadduct **4** and 65% unreacted bis-adduct **3**, whereas CPE after the second reduction wave (arrow D, Figure 4) resulted in 5% C₆₀, 30% monoadduct **4**, and 19% bis-adduct **3**. The regioisomer distribution of the bis-adducts isolated in these electrolyses was very similar to that found for the starting material **3**.

CPE of **5** after the third reduction wave discharged 4.7 electrons and yielded, after reoxidation, purification and characterization 65% of C₆₀.⁶

Thus, adduct removal is a very general reaction, which occurs for **1** and **3–5**. Furthermore, a secondary reaction pathway with the solvent is observed for **1**, **2** and **6**. This

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(18) We attempted to prove the presence of chlorine in these structures by the isotope pattern in the Maldi-Tof spectrum (³⁵Cl/³⁷Cl = 76:24). However, as was shown by simulations, the dominating factor in the isotope pattern for these molecules is not chlorine but the high number of carbons (1-CH₂Cl contains 72 carbons), rendering the identification of chlorine by Maldi-Tof somewhat ambiguous.

(19) CPE at even more negative potentials leads to uncontrolled reactions; no fullerene products could be isolated after reoxidation.

(20) Monitoring of the CPE-experiment by electrochemical (CV, OSWV) and ESR measurements normally requires a period of 30–60 min. between the reductive electrolysis and the oxidative electrolysis.

Table 2. Results of CPE at Methanofullerenes 1–6 in the Solvents Dichloromethane and THF

| | total yield CPE (%) | C ₆₀ (%) | starting material (%) | other products (%) |
|----------|------------------------------------|---------------------|--------------------------|--|
| DCM | | | | |
| 1 | 38 | 19 | | 19 (1 -CH ₂ Cl) |
| 2 | 58 | | 29 | 29 (2 -CH ₂ Cl) |
| 3 | 70 ^a 75 ^b | 35 75 | | 35 (monoadduct 4) |
| 4 | 80 | 58 | 22 | |
| 5 | 65 | 65 | | |
| 6 | 60 | | | 60 (6 -CH ₂ Cl) |
| THF | | | | |
| 1 | 32 | 32 ^e | | |
| 2 | 50 | | 50 ^e | |
| 3 | 80 ^a 30 ^b | 14 14 | 33 | 33 (monoadduct 4) 16 (monoadduct 4) |
| 4 | 81 ^a 84 ^b | 40 35 | 27 30 | 14 (bis-adduct 3) ^c 19 (bis-adduct 3) ^d |
| 5 | 91 | 41 | 39 | 11 (bis-adduct of 5) |

^a Electrolysis after first reduction wave. ^b Electrolysis after second reduction wave. ^c *trans*-2, 3%; *trans*-3, 7%, ee 37%; *cis*-3, 49%. ^d *trans*-2, 6%; *trans*-3, 11%, ee 43%; *cis*-3, 37%. ^e Main product, not totally pure.

confirms that dichloromethane is not a good solvent for electrochemical measurements of fullerenes.¹⁷ On the basis of these observations, it was decided to investigate the electrochemical behavior of the methanofullerenes in the less reactive solvent THF.

Electrochemistry in THF. The CVs of the methanofullerene derivatives in the solvents dichloromethane and THF are very similar. Electrolysis of **1** at the same potential as shown by arrow A in Figure 4 discharged 2.7 electrons. Reoxidation of the electrolysis mixture yielded fullerene products in a 32% yield, mainly consisting of C₆₀.

Electrolysis of **2** was performed after the third reduction wave, as indicated by arrow B in Figure 4 for DCM, and it discharged 2.5 electrons. Essentially no changes were observed in the cyclic voltammogram, and reoxidation and purification yielded 50% of fullerene products, mainly recovery of the starting material.

Previously, we reported that electrolysis of **4** and **5** in THF resulted in clean adduct removal and formation of C₆₀. However, an alternative reaction pathway also led to the formation of bis-adducts for **4** and **5**, but not for the other compounds. The formation of bis-adducts from the electrolysis of **4** was easily proven by comparison with the synthetically prepared bis-adducts **3**. The formation of bis-adducts for **5** was proven by HPLC and Maldi-Tof.²¹ Detailed studies showed that electrolysis of **4** after the first or after the second reduction wave yielded mainly the *e* and *cis*-3 regioisomeric bis-adducts (see Table 2). The formation of the *cis*-3 regioisomer in such a high percentage is unprecedented in fullerene derivative synthesis, except when it is selected using the tether-directed remote functionalization method, designed for that particular isomer.²² We have tentatively proposed a mechanism that involves the presence of fullerene-dimer²³ intermediates to rationalize these observations.⁸

(21) Main peaks in Maldi-Tof spectrum at 1004 (bis-adduct), 912, and 720 amu. Maldi-Tof spectra for fullerenes always shows fragmentation in the mass-spectrometer (720 amu = C₆₀; 912 = mono-adduct **5**). HPLC measurements show that the sample itself does not contain any of these two fragments.

(22) Nierengarten, J.-F.; Habicher, T.; Kessinger, R.; Cardullo, F.; Diederich, F.; Gramlich, V.; Gisselbrecht, J.-P.; Boudon, C.; Gross, M. *Helv. Chim. Acta* **1997**, *80*, 2238–2276.

The mechanism was supported by molecular modeling studies.

CPE of isomers **3** after the second wave discharged 3.0 electrons. Reoxidation and purification yielded 30% fullerene products, consisting of 14% C₆₀ and 16% mono-adduct **4**. CPE after the first reduction wave discharged 2.0 electrons and yielded, after reoxidation and purification, 14% of C₆₀, 33% monoadduct **4**, as well as 33% of bis-adducts **3**. No tris-adducts were isolated. The regioisomer distribution of the recovered bis-adducts **3** had changed considerably in comparison with the starting material, with an increase of the *cis*-3 isomer from 5% to 13%. This apparent isomerization, which favors the *cis*-3 regioisomer, can follow an intermolecular (via the mono- or tris-adduct) or intramolecular pathway. Currently we are investigating the mechanism of this isomerization.

Conclusions

In conclusion, we have synthesized several new methanofullerene derivatives by the diazomethane route. Assignment of the regioisomers of the bis-adduct **3** were made by ¹H NMR, UV-vis, and HPLC. These methanofullerenes exhibit interesting electrochemistry in dichloromethane and THF. Reductive electrolysis of the methanofullerene **1** and **3–5** in dichloromethane leads to removal of the addends to form C₆₀. This could be used as a protective group in synthetic fullerene chemistry. Interestingly, an alternative reaction pathway was observed for **1**, **2**, and **6**, which leads to the formation of methanofullerene-CH₂Cl products of unspecified structure. Reductive electrolyses in THF shows clean adduct removal for **1** and **3–5**. Another reaction pathway was observed in THF for **4** and **5**, an intermolecular addend crossover reaction leading to bis-adducts. We are currently investigating the mechanisms and possible applications of these new electrochemical reactions.

Experimental Section

General Details. ¹H NMR and ¹³C NMR spectra were obtained using a Varian VXR-300, a Bruker Avance-300, and a Bruker AMX-500. Mass spectra were recorded using a VC Autospec EBE spectrometer operating at 30 kV by using a bombardment of Cs⁺ ions and 2-NPOE or 3-NBA as matrix or Maldi-Tof MS: PerSeptive Biosystems Voyager-DE STR spectrometer. FTIR spectra were recorded using a Nicolet Magna-IR spectrometer 5550. UV-vis: Shimadzu UV 2101 PC spectrometer. HPLC: Varian ProStar with a SiO₂ column. All chromatography was performed using Merck silica gel (70–230 mesh). All reagents were used as purchased unless otherwise stated. All solvents were dried according to standard procedures.

Electrochemistry. Details of the experimental electrochemical setup for the CV, Osteryoung square wave voltammetry (OSWV), and bulk electrolysis measurements have been described elsewhere.²⁴ Briefly, electrochemical measurements were performed using a BAS 100W electrochemical analyzer (Bioanalytical systems). An electrochemical cell designed to carry out CV, OSWV, and bulk electrolysis under high vacuum was used. For CV and OSWV, a glassy-carbon working electrode, a silver wire pseudoreference electrode, and a Pt-mesh counter electrode were used. Bulk electrolysis was carried out using Pt mesh electrodes for both working and counter electrode. As supporting electrolyte, tetrabutylammo-

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nium hexafluorophosphate was used. Dichloromethane was distilled over silica, THF over Na/K before use.

Materials. We previously reported the synthesis of the methanofullerenes **5** and **6**.^{7d}

Preparation of Diazo Compounds 7–9. 3-Methyl-1-diazonaphthalene-4-oxide (**7**) was prepared from 2-methyl-1,4-naphthoquinone by reaction with *p*-tosylhydrazine and subsequent base-catalyzed decomposition.¹⁰ 3,5-Diphenyl-1-diazobenzene-4-oxide (**8**) was obtained by reaction of 2,6-diphenyl-1,4-benzoquinone similarly to **7**.¹¹ 2-Diazo-1,3-indandione (**9**) was prepared from 1,3-indandione and tosyl azide at low temperature according to the procedure reported in the literature.¹² The diazo compounds **7–9** were used immediately in the next step.

Spiro[1'(5'-methylbenzocyclohexadien-4'-one)-1',61-methano[60]fullerene] (1). To a solution of C₆₀ (177 mg, 0.25 mmol) in *o*-dichlorobenzene (15 mL) was added 3-methyl-4-oxodiazonaphthalene¹⁰ (**7**, 50 mg, 0.27 mmol), and the reaction mixture was irradiated with a sun lamp at 0–10 °C under argon atmosphere for 3 h. The solvent was removed under reduced pressure. The resulting solid was purified by silica gel chromatography using cyclohexane/toluene 1/1 as eluent: 17% yield (34% based on consumed C₆₀); FTIR (KBr) ν/cm^{-1} 1664, 1661, 1659, 1459, 1185, 765, 714, 587, 526; ¹H NMR (300 MHz, CDCl₃) δ 2.37 (d, 3H, *J* = 1.5 Hz), 7.67 (dt, 1H, *J* = 7.7, 1.1 Hz), 7.76 (dt, 1H, *J* = 7.7, 1.8 Hz), 8.41 (d, 1H, *J* = 1.5 Hz), 8.50 (dd, 1H, *J* = 7.7, 1.8 Hz), 9.14 (dd, 1H, *J* = 7.7, 1.1 Hz); ¹³C NMR (75 MHz, CDCl₃/CS₂) δ 29.8, 40.6, 77.2, 78.4, 125.4, 128.5, 128.7, 131.9, 134.0, 137.7, 138.7, 138.8, 139.2, 139.9, 140.0, 141.1, 141.3, 141.6, 142.1, 142.2, 143.1, 143.2, 143.3, 143.9, 144.0, 144.5, 144.7, 144.8, 144.9, 145.0, 145.3, 145.4, 147.3, 148.3, 184.6; MS *m/z* 876 (M⁺, 19), 720 (C₆₀, 100); UV–vis (CHCl₃) $\lambda_{\text{max}}/\text{nm}$ 258, 282, 322, 436, 690.

Spiro[1'(3',5'-diphenylcyclohexadien-4'-one)-1',61-methano[60]fullerene] (2). To a solution of C₆₀ (156 mg, 0.22 mmol) in dry *o*-dichlorobenzene (15 mL) was added 3,5-diphenyl-4-oxadiazobenzene¹¹ (**8**, 80 mg, 0.29 mmol), and the reaction mixture was irradiated with a sun lamp at 0–10 °C under argon atmosphere for 2.5 h. Flash chromatography of the reaction mixture, using cyclohexane/toluene 1/1 as eluent, gave pure adduct: 17% yield (84% based on consumed C₆₀); FTIR (KBr) ν/cm^{-1} 649, 1625, 897, 816, 737, 714, 697, 525; ¹H NMR (300 MHz, CDCl₃) δ 7.47–7.55 (m, 6H), 7.72–7.74 (m,

4H), 8.21 (s, 2H); ¹³C NMR (75 MHz, CDCl₃/CS₂) δ 40.8, 77.2, 128.2, 128.3, 128.5, 129.1, 129.3, 129.8, 132.2, 135.6, 137.1, 138.3, 141.9, 142.0, 142.9, 143.5, 143.9, 144.7, 144.8, 144.9, 145.0, 145.4, 146.0, 147.0, 185.7; MS *m/z* 964 (M⁺, 20), 720 (C₆₀, 100); UV–vis (CHCl₃) $\lambda_{\text{max}}/\text{nm}$ 258, 328, 436.

Spiro[1'(2',7'-indandione)-1',61-methano[60]fullerene] (4). An *o*-dichlorobenzene solution of C₆₀ (100 mg, 0.138 mmol) and 2-diazo-1,3-indandione¹² (**9**, 478 mg, 0.27 mmol) was heated to reflux under argon atmosphere for 4 h. The solvent was removed under reduced pressure, and the crude material was carefully chromatographed on a silica gel column using cyclohexane/toluene 1/1 as eluent. Unreacted C₆₀ eluted first, followed by the monoaddition product (**4**), and finally, the regioisomeric mixture of the bis-adducts **3** was obtained. Further purification was accomplished by repetitive precipitation and centrifugation using hexane, methanol, and diethyl ether as solvents.

Spiro[1'(2',7'-indandione)-1',61-methano[60]fullerene] (4): 43% yield (62% based on consumed C₆₀); FTIR (KBr) ν/cm^{-1} 1712, 1515, 1503, 1264, 1228, 744, 711, 698, 526; ¹H NMR (300 MHz, CDCl₃) δ 8.22–8.15 (m, 2H), 8.02–7.95 (m, 2H); ¹³C NMR (125 MHz, CDCl₃/CS₂ 1/1) δ 64.4, 74.1, 123.3, 135.8, 140.9, 141.4, 141.5, 141.7, 142.1, 142.9 (2C), 143.0, 143.6, 143.8, 144.4, 144.5, 144.6, 144.7, 144.9, 145.1, 191.0; MS *m/z* 864 (M⁺, 55), 720 (C₆₀, 80); UV–vis (CHCl₃) $\lambda_{\text{max}}/\text{nm}$ 290, 338, 432, 510, 660.

Bis [1'(2',7'-indandione)-1',61-methano[60]fullerenes] (3): 10% yield (13% based on consumed C₆₀); FTIR (KBr) ν/cm^{-1} 1716, 1593, 1458, 1378, 1350, 1323, 1231, 1044, 939, 792, 780, 755, 740, 722, 698, 525; ¹H NMR (300 MHz, CDCl₃) δ 8.31–7.85 (m, 8H); MS *m/z* 1009 (M⁺, 100), 864 (**4**, 16); UV–vis (CH₂Cl₂) $\lambda_{\text{max}}/\text{nm}$ 250, 282, 314, 428, 482.

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