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Electroreductive retro-cyclopropanation reactions of nitrophenyl-methanofullerene derivatives†

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Spiromethanofullerenes **5**, **8** and **10** containing a nitrophenyl substituent attached to the methano adduct, were synthesized *via* the diazomethane route or *via* the Bingel reaction. The electrochemistry and electrolysis of these compounds were investigated in THF. Reductive electrolysis leads to the removal of the addend, formation of [60]fullerene, and to the formation of bis-adducts from the mono-adducts. The extent of the retro-cyclopropanation reaction varied as a function of the structural and electronic differences between the compounds. Electron spin resonance studies (ESR) allowed the observation of spin localization on the fullerene core or on the nitrobenzene moiety upon successive reductions.

Introduction

The addition of bis(ethoxycarbonyl)methylene units [$C(CO_2Et)_2$] to C_{60} is readily achieved by treatment of [60]fullerene with diethyl bromomalonate under Bingel reaction conditions.[1] Cyclopropane rings fused to the carbon sphere have generally been found to be highly stable,[2] although, some exceptions were reported.[3–5] Recently, Diederich and Echegoyen discovered that exhaustive controlled potential electrolysis (CPE) of these fullerene-Bingel adducts leads to the efficient removal of the cyclopropane ring from the carbon sphere to yield predominantly C_{60}.[6] This process was called the retro-Bingel reaction and has been successfully employed to remove up to four di(alkoxycarbonyl) methano groups from a variety of cyclopropane adducts of C_{60}, C_{70}, C_{76} as well as C_{2v} and D_3-C_{78}.[6,7] Additionally, this protocol has made possible the isolation of new isomers of C_{84} and of a novel C_{78} bis-adduct.[8,9] Interestingly, it was also observed that partial electrolysis of bis- or tris-Bingel adducts of C_{60} results in isomerization of the adducts.[10] The recent development of the chemical retro-Bingel process, using Mg/Hg in THF at elevated temperatures,[11] has expanded the utility of the Bingel-[retro-Bingel] strategy as part of a protection–deprotection protocol in the synthesis of non-Bingel adducts with unusual addition patterns.[12]

Addend removal *via* electrolytic or chemical reduction is not limited to Bingel-type adducts,[13] and can also occur for spiromethanoadducts such as those depicted in Fig. 1. We have shown that controlled potential electrolysis (CPE) in dichloromethane results in the efficient removal of these adducts to form the parent C_{60}.[14] Interestingly, an alternative reaction pathway was observed for **3** (Fig. 1) which leads to the formation of methanofullerene-CH_2Cl products of as yet unspecified structure.[15] Exhaustive reductive electrolysis in THF leads also to efficient adduct removal, but an alternative reaction pathway was observed in THF for **1** and **2** (Fig. 1) that led to the formation of bis-adducts.[16]

In order to investigate the mechanism, characterize the electroreduced intermediates, and explore the possible applications of these new electrochemically-induced reactions, compounds **5**, **8** and **10** were prepared. These compounds have as a common characteristic the nitrophenyl group, which when reduced exhibits a strong and easily recognizable ESR signal. The spectroscopic, cyclic voltammetric, bulk electrolysis and ESR properties of these compounds are discussed in this article.

Results and discussion

Synthesis

Compounds **5**, **8** and **10**, which incorporate a nitrophenyl containing addend, were designed with varying electron-withdrawing substituents in order to test their effect on the efficiency of the electrolytic removal of the addend.[12] The synthesis of the spiromethanofullerenes **5** and **8** was carried out by reaction of [60]fullerene with the respective diazo compounds by heating in 1,2-dichlorobenzene (ODCB) under an argon atmosphere (Scheme 1).[17]

The starting hydrazone **4**[18] was prepared by the Bamford–Steven reaction from the respective carbonyl derivative and *p*-tosylhydrazide. Further treatment of **4** under basic conditions generates "*in situ*" the diazo compound which readily

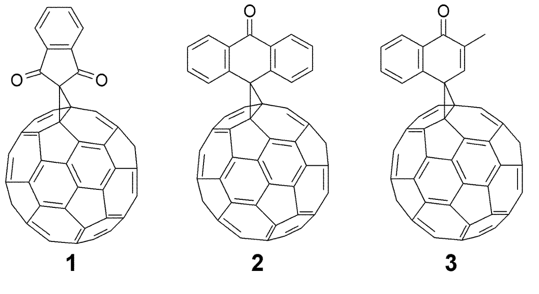

Fig. 1 Representative examples of spiromethanofullerenes studied by reductive electrochemistry.

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†Dedicated to Professor Waldemar Adam on the occasion of his 65th birthday.

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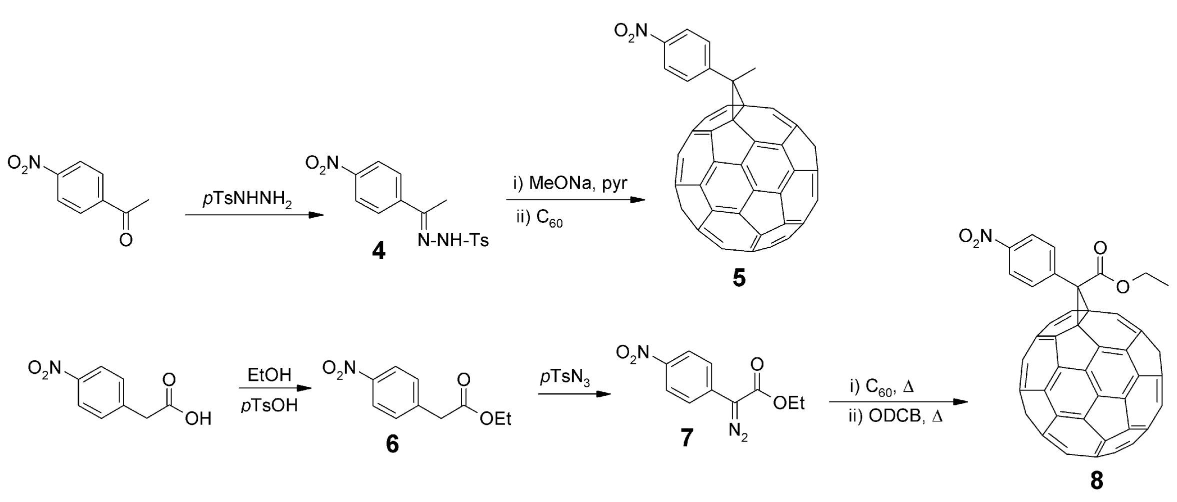


Scheme 1 Synthesis of novel spiromethanofullerenes from diazo compounds.

undergoes the 1,3-dipolar cycloaddition to C_{60} to form methanofullerene **5**. Diazo compound **7** was prepared from the ester **6** by reaction with *p*-tosylazide[19] following the experimental procedure previously reported in the literature.[20]

Ethyl 4-nitrobenzoylacetate (commercially available) was used as precursor for the synthesis of **10**. Although the corresponding diazo compound was generated by reaction with *p*-tosylazide, it did not react with the [60]fullerene either by irradiation under a sun lamp or by heating in ODCB or toluene. As an alternative procedure compound **10** was synthesized following a Bingel protocol. When the reaction was carried out in the presence of CBr_4–DBU, **10** was only isolated in trace amounts and **9** was the predominant product. Under the conditions depicted in Scheme 2 (I_2–DBU), **10** was obtained in a 16% yield (25% based on recovered C_{60}).

The compounds were characterized using spectroscopic techniques. The UV-Vis spectra showed a typical absorption peak at around 430 nm characteristic of [6,6]closed methanofullerenes. The ^{13}C NMR spectra of these derivatives show the presence of the cyclopropane carbons in the region between 74 and 46 ppm, and the large number of peaks obtained denotes the lack of symmetry in these structures. The FTIR, MALDI-TOF and ^1H NMR spectra were also consistent with the assigned structures.

Electrochemistry

We have demonstrated recently that the commonly used electrochemistry solvent dichloromethane reacts readily with the trianion of C_{60}.[21] This reaction gave methanofullerenes $C_{60}{>}(CH_2)_n$ (with n = 1–4). Consequently, dichloromethane should be used only with extreme caution as a medium in which to do the electrochemistry of fullerenes. For this reason, we decided to investigate the electrochemical behavior of the compounds in the less reactive solvent THF.

The electrochemistry of **5**, **8** and **10** was studied by cyclic voltammetry (CV) and by Osteryoung square wave voltammetry (OSWV). Potentials *vs.* ferrocene are reported in Table 1, and the cyclic voltammograms for **8** and **10** are presented in Fig. 2. The electrochemical behavior of **5** and **8** is

Table 1 Redox potentials of methanofullerenes **5**, **8**, and **10** *vs.* ferrocene in THF (mV)

Compound	E^1_{red}	E^2_{red}	E^3_{red}	E^4_{red}
5	−957	−1508	−1721	−2174
8	−913	−1483	−1684	−2127
10	−903	−1390	−1689	−1870[a]

[a] Electrochemically irreversible reduction, oxidation wave at −1069 mV.

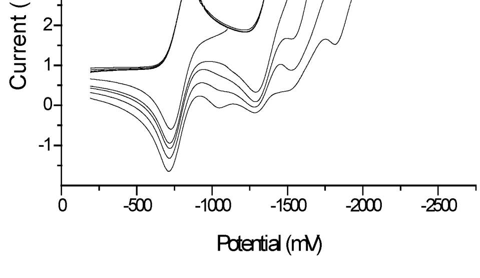
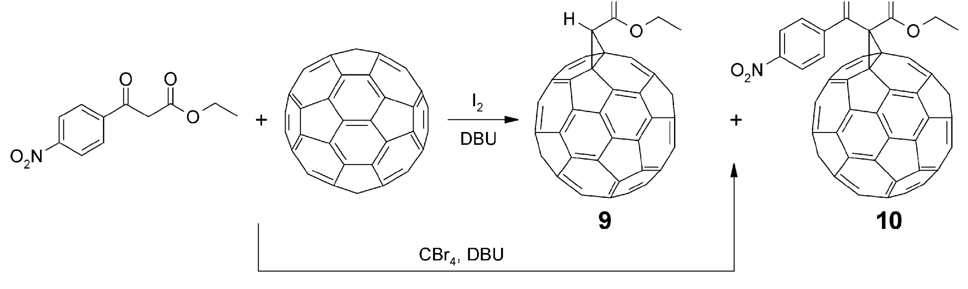


Fig. 2 Cyclic voltammograms *vs.* ferrocene for **8** and **10** in THF.



Scheme 2 Synthesis of the spiromethanofullerene **10** following a Bingel procedure.

Table 2 Results of CPE at methanofullerenes **5**, **8** and **10** in THF

	Total yield CPE (%)	C_{60} (%)	Starting material (%)	Other products (%)
5	45	5	40	–
8	81	23	40	18 (Bis-adducts)
10	100	52	37	11 (Bis-adducts)

very similar, exhibiting three reversible fullerene reductions[22] and one reversible nitrobenzene reduction. **10** exhibits more chemical irreversibility (Fig. 2).

Typically each compound was subjected to controlled potential electrolysis (CPE) at a potential *ca.* 100–150 mV more cathodic than every reduction wave and then analyzed by ESR spectroscopy. Reoxidation at 0 V was usually performed after bulk electrolysis at the third or fourth reduction potential followed by analysis of the products (Table 2).

CPE of methanofullerene **5** after the first and second reduction waves shows no changes in the CV or OSWV. Subsequent electrolysis after the third reduction consumed *ca.* 3 electrons molecule^{-1}, and also no appreciable changes in the CV or OSWV were observed. After reoxidation and purification, analysis of the reaction mixture by HPLC and MALDI-TOF showed the formation of a small amount of C_{60} (5%) and recovery of 40% of the starting material.

Electrolysis of **8** was performed also after the first, second and third reduction waves. Reoxidation at 0 V and purification after the third reduction wave resulted in 81% fullerene products, consisting of 23% C_{60}, 40% starting material, and 18% bisadducts (determined by HPLC and MALDI-TOF), similar to previous observations.[15,16] In a separate experiment, electrolysis was carried out after the fourth reduction wave but reoxidation and purification resulted in the formation of insoluble products.

CPE of methanofullerene **10** after the fourth reduction consumed 5.5 electrons molecule^{-1} and induced clear changes in the CV and OSWV, indicating that a chemical reaction had taken place. Subsequent reoxidation at 0 V and purification of the product mixture by column chromatography (eluent: toluene) yielded fullerene products in *ca.* quantitative yield. Analysis of this mixture showed 52% of C_{60}, 11% of bis-adducts (MALDI-TOF and HPLC confirmation) and 37% of an as yet uncharacterized material.

It should be noted that when electrolyses are performed and immediately followed by reoxidations (no sampling times for ESR observations), the degree of the retro-cyclopropanation reaction is pronouncedly decreased. This clearly indicates that the retro-Bingel process proceeds with relatively slow kinetics following the corresponding reductions.

ESR experiments

In order to probe the sites of reduction and to monitor the reactive intermediates resulting from subsequent reductions, samples were quantitatively electrolyzed at different controlled potentials and then analyzed by ESR spectroscopy.

ESR spectra recorded during the electrolysis of **5** showed that the first and second reduction electrons are mainly localized on the fullerene unit (Fig. 3).[23] Spectrum 3(a), corresponding to the one-electron reduction species, clearly shows fullerene-based signals, with *g* factors of 2.00238 and 2.00086. The di-reduced species also show a paramagnetic signal that is fullerene-based with a *g* factor of 2.00243.[23] Addition of the third electron changes the appearance of the overall ESR-spectrum, and the pattern clearly shows a nitrophenyl-based radical, with a *g* factor of 2.00522. For the nitrophenyl unit a triplet of triplet of triplets (ttt) is observed.[24] The coupling constants measured are: $a_N = 9.55$ G, $a_o = 3.25$ G and $a_m = 0.91$ G and correspond to one nitrogen and two sets of two equivalent protons.[24] The simulated spectrum corresponding to this radical is also shown in Fig. 3(d). The fullerene-based signal disappears completely as this nitrophenyl-based signal increases. It is important to note that the nitrophenyl signal does not correspond to that of the free nitrobenzene anion radical, since the *para* hydrogen splitting is not observed. Ever since Maki and Geske studied the nitrobenzene anion radical in solution[25] many investigations have been carried out with this radical, which shows pronounced environmental effects due to solvent and counterion interactions.[24] The reported coupling constants for the nitrobenzene anion radical in acetonitrile media are $a_N = 10.32$ G, $a_o = 3.97$ G, $a_m = 3.39$ G and $a_p = 1.09$ G.[25]

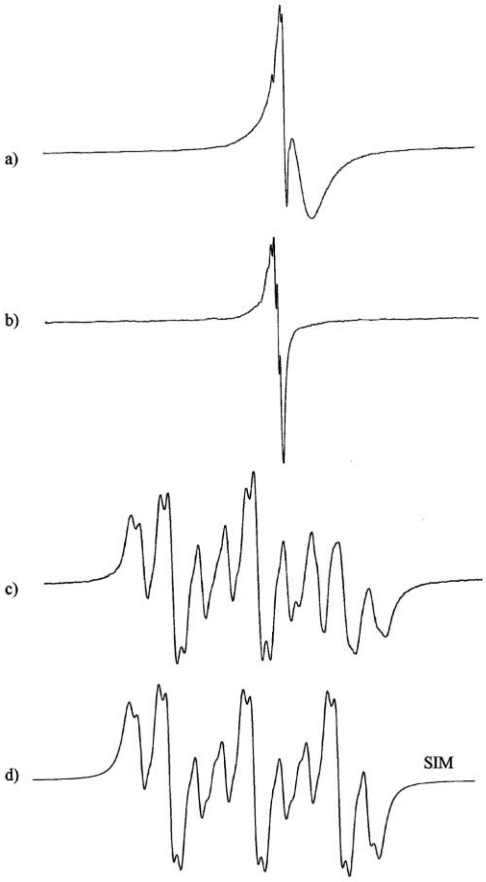


Fig. 3 ESR spectra for the sequential electrolytic reduction of **5** in THF. (a) After one-electron coulometric reduction, (b) after two-electron-reduction, (c) after three-electron reduction, and (d) computer simulation of the nitrophenyl-based signal. The parameters used for this simulation are: $a_N = 9.55$ G, $a_o = 3.25$ G and $a_m = 1.02$ G, linewidth = 0.95 G.

Fig. 4 shows the sequence of the ESR spectra observed during the electrolysis of compound **8**. The first two spectra are typically fullerene-based radicals and have *g* factors of 2.00191 and 2.00139 respectively.[23] After the third reduction, the observed ESR spectrum shows the presence of two radical species, where the sharp signal on the right has a *g* value of 2.00265 and indicates the presence of some $C_{60}{}^{3-}$. The other ESR signal, centered at a *g* factor of 2.00522, is apparently due to the nitrophenyl-based radical anion and consists of a triplet of triplet of triplets (ttt) with coupling constants of $a_N = 9.15$ G, $a_o = 3.35$ G and $a_m = 1.03$ G, similar to the ones obtained for compound **5**. The simulated spectrum is shown in Fig. 4(d) and fits the experimental data well. Interestingly, after five-electron reductions, the nitrophenyl-based signal disappeared leaving an ESR signal identical to the one observed after the three-electron reduction (*g* factor = 2.00268). This observation probably indicates the presence of the trianion of

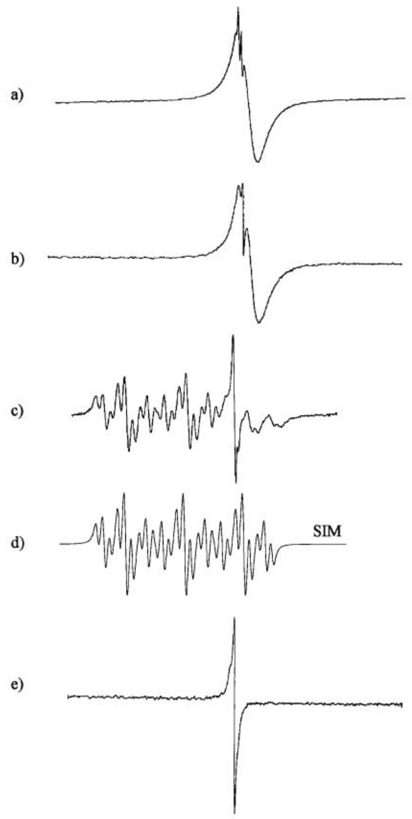


Fig. 4 ESR spectra for the sequential electrolytic reduction of **8** in THF. (a) After one-electron coulometric reduction, (b) after two-electron-reduction, (c) after three-electron reduction, (d) computer simulation for the three-electron reduction spectrum. The parameters used for this simulation are: $a_{\mathrm{N}} = 9.15$ G, $a_o = 3.35$ G and $a_m = 1.02$ G, linewidth = 0.50 G, and (e) after four-electron reduction.

C_{60} and a diamagnetic dianion on the nitrobenzene-addend part.

The ESR analysis of compound **10** was carried out in a similar way. Fig. 5(a) shows the ESR spectrum of compound **10** after electrolysis with one electron. This radical species has a *g* value of 2.00008. After three-electron reduction, the ESR spectrum shows the presence of both nitrophenyl and fullerenyl radicals, with *g* factors of 2.00471 and 2.00105 respectively. The estimated coupling constants in the *p*-nitrophenyl-based radical are $a_{\mathrm{N}} = 7.35$ G, $a_o = 2.96$ G and $a_m = 0.81$ G. The simulated spectrum is shown in Fig. 5(c) and it reproduces exactly the ESR behavior of this *p*-nitrophenyl-based radical. The effect of the electron-withdrawing ketone group in the *para* position is responsible for the much lower a_{N} value observed when compared to that for compounds **5** and **8**. This is the expected result, since the charge and spin density on the NO_2 group is reduced as a consequence of the *para* substituent.[26] Analogous cases have been reported, for example $a_{\mathrm{N}} = 7.15$ G for a *p*-CN substituent and $a_{\mathrm{N}} = 7.02$ G for a *p*-$COCH_3$.[25,26] When the electrolysis is carried out further for a total of four electrons, a modified nitrophenyl-based radical dominates the spectrum. It shows four coupling constants with: $a_{\mathrm{N}} = 9.18$ G, $a_o = 3.26$ G, $a_m = 1.02$ G and an additional doublet splitting of 0.40 G. Why the a_{N} value changes from 7.02 G to 9.18 G is not presently understood, but it has been amply documented that this hyperfine coupling constant is very sensitive to solvent and counterion effects.[25,26]

The simulated spectrum using these coupling constants is shown in Fig. 5(e). It clearly shows that the radical generated contains a single spin ½ nucleus, most probably a proton, which exhibits a hyperfine coupling constant of 0.40 G. A possible structure for this radical intermediate is shown in Scheme 3. This seems like a reasonable intermediate based on the previously reported value of $a_{\mathrm{Me}} = 0.66$ G for the 4-nitroacetophenone.[25] Exactly how this transformation takes place is not presently known in detail, but it fits well with the ESR observations and with the known formation of C_{60} *via* the retro-Bingel reaction as a final product after reoxidation. Studies are underway to elucidate the mechanistic details of these reactions.

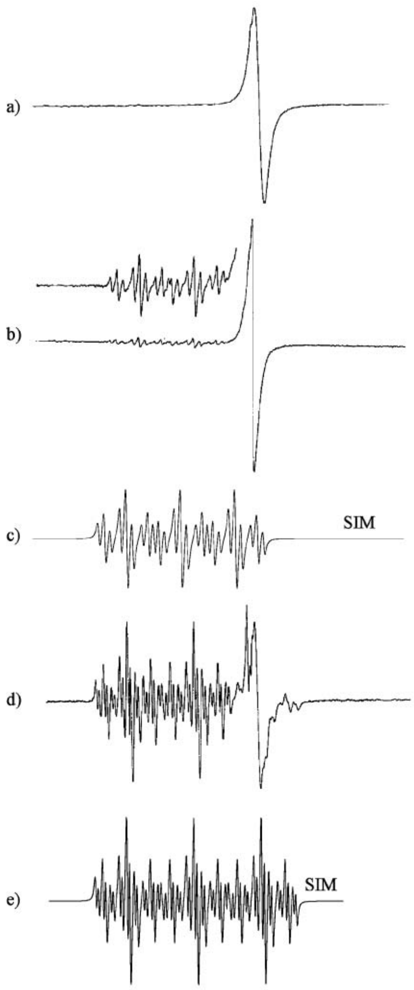
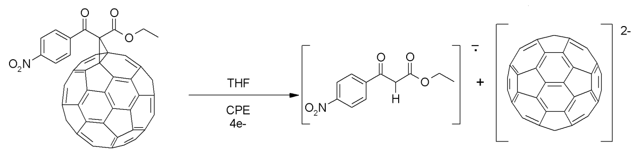


Fig. 5 ESR spectra for the reduction of **10** in THF. (a) After one-electron coulometric reduction, (b) after three electrons, (c) computer simulation of the *p*-nitrophenyl-based signal after three-electron reduction. The parameters used for this simulation are: $a_{\mathrm{N}} = 7.35$ G, $a_o = 2.96$ G and $a_m = 0.81$ G, linewidth = 0.30 G, (d) four electrons, and (e) computer simulation of the *p*-nitrophenyl-based signal after four-electron reduction. The parameters used for this simulation are: $a_{\mathrm{N}} = 9.18$ G, $a_o = 3.26$ G, $a_m = 1.02$ G and $a_H = 0.40$ G, linewidth = 0.20 G.



10

Scheme 3 Possible intermediate identified *via* ESR spectral simulation during the electrolytic retro-Bingel reaction of **10**.

Experimental

General methods and procedures

^{1}H NMR and ^{13}C NMR spectra were obtained using a Varian VXR-300 and a Bruker Avance-300. Mass spectra were recorded using a MALDI-TOF MS: Perspective Biosystems Voyager-DE STR spectrometer. FTIR were recorded using a Nicolet Magna-IR spectrometer 5550. UV-Vis: Shimadzu UV 2101 PC spectrometer. HPLC: Varian Prostar with a SiO_2 column. 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: electrochemical measurements were performed using a BAS 100 W electrochemical analyzer. Fullerene mono-adducts (2–3 mg) and supporting electrolyte Bu_4NPF_6 (0.6 g) were added into a home-built two-compartment electrolysis cell (for full description see reference 27). The cell was degassed and pumped to 10^{-6} mmHg. The solvent, THF (8 mL), which had also been degassed and pumped to the same pressure, was then vapor-transferred into the cell, directly from Na/K. Prior to the CPE, cyclic voltammetry was performed using a glassy carbon electrode to obtain the reduction potential *vs.* a Ag wire pseudo-reference electrode. The latter was separated from the bulk solution using a vycor tip. CPE at 293 K was performed on a Pt mesh (100 mesh, 6.5 cm^2) working electrode. After reductive electrolysis, the solution was re-oxidized at 0 V *vs.* Ag. The electrolyte was removed by evaporation of the solvent followed by product extraction with toluene. The product mixture was then passed through a short column of SiO_2 and eluted with toluene. TLC, HPLC, MALDI-TOF spectrometry, ^1H NMR and/or UV-Vis were used to identify the products.

ESR experiments. ESR samples were obtained in sealed 3-mm o.d. Pyrex tubes that were directly attached to the electrochemical cell. After exhaustive electrolysis with the BAS 100 W apparatus at different potentials corresponding to the various anionic states, the cell was tilted in order to collect a sample in the ESR tube. The solution, after recording the spectrum, was poured into the cell again in order to continue the electrolysis process. The samples were analyzed using the X-band of a Bruker ER 200 SRC ESR spectrometer.

Computer simulations were performed on PC computer using the WIN EPR program from NIEHS (USA).

1′-Methyl-1′-(4-nitrophenyl)-1,2-methano[60]fullerene (5)

To a solution of tosylhydrazone **4**[18] (67 mg, 0.2 mmol) in 1.6 mL of pyridine (previously dried with KOH), MeONa (12 mg, 0.22 mmol) was added under an argon atmosphere. After 15 minutes with stirring, a previously prepared C_{60} solution (144 mg, 0.2 mmol) in 10 mL of ODCB was added. This mixture was heated under reflux for 20 hours and monitored by TLC in cyclohexane–toluene (1 : 1). The solvent volume was concentrated *in vacuo* and was then loaded on a silica gel column and eluted with cyclohexane–toluene (1 : 1). The product was recovered as a mixture of the [5,6] and [6,6] isomers in a 39% yield. The rearrangement of the [5,6] open fulleroid to the [6,6] closed methanofullerene occurs by refluxing the mixture in *o*-dichlorobenzene (ODCB) for 24 hours in quantitative yield. Further purification was carried out by repetitive precipitation and centrifugation using methanol and diethylene oxide as solvents. The spectroscopic data for compound **5** agree with those in the literature.[28] FTIR (KBr) ν 2922, 1599, 1517, 1427, 1341, 852, 698, 526 cm^{-1}; ^1H NMR ($CDCl_3$–CS_2 1 : 2, 300 MHz) δ 8.43 (d, 2H, J = 8.6 Hz), 8.19 (d, 2H, J = 8.6 Hz), 2.60 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$–CS_2 1 : 2, 75 MHz) δ 147.49, 147.45, 146.88, 146.37, 145.38, 145.11, 145.06, 144.98, 144.71, 144.66, 144.60, 144.57, 144.41, 144.39, 144.36, 144.06, 143.59, 143.57, 143.01, 142.96, 142.94, 142.93, 142.91, 142.05, 142.01, 141.83, 141.01, 140.85, 138.05, 137.22, 131.73, 130.38, 127.51, 123.91, 79.55, 46.03, 21.97; UV-vis ($CHCl_3$), λ_{max} 261, 327, 430; *m*/*z* (MALDI-TOF) 869 (M^+).

1′-Ethoxycarbonyl-1′-(4-nitrophenyl)-1,2-methano[60]fullerene (8)

A mixture of ethyl diazo(4-nitrophenyl)acetate **7**[20] (306 mg, 1.30 mmol) and C_{60} (937 mg, 1.30 mmol) in ODCB (70 mL) was refluxed for 3 hours. The solvent was removed under reduced pressure and the solid residue thus obtained was purified by column chromatography on silica gel, using CS_2 to elute unreacted C_{60} and cyclohexane–toluene 1 : 1 to elute compound **8** as a mixture of the [5,6] and [6,6] isomers in a 32% yield (64% based on recovered C_{60}). Further isomerization to the more stable methanofullerene was accomplished by refluxing the isomer mixture in ODCB for 24 hours, obtaining the [6,6] isomer in quantitative yield. Additional purification of this product was carried out by repetitive precipitation and centrifugation using methanol and diethylene oxide as solvents. FTIR (KBr) ν 2963, 1741, 1629, 1517, 1513, 1443, 1344, 1261, 1227, 1185, 1092, 1023, 802, 525 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.42 (d, 2H, J = 8.9 Hz), 8.31 (d, 2H, J = 8.9 Hz), 4.44 (q, 2H, J = 7.1 Hz), 1.39 (t, 3H, J = 7.1); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.87, 148.08, 146.21, 145.08, 145.04, 144.96, 144.72, 144.59, 144.58, 144.51, 144.47, 144.40, 144.15, 143.72, 143.48, 142.98, 142.96, 142.90, 142.84, 142.70, 141.99, 141.97, 141.94, 141.62, 140.96, 140.90, 139.10, 138.06, 137.87, 133.10, 123.58, 74.53, 63.23, 54.06, 14.25; UV-vis ($CHCl_3$), λ_{max} 260, 326, 428, 490, 690, 828; *m*/*z* (MALDI-TOF) 928 (M^+).

1′-Ethoxycarbonyl-1′-(4-nitrobenzoyl)-1,2-methano[60]fullerene (10)

To a solution of C_{60} (210 mg, 0.29 mmol), I_2 (90 mg, 0.35 mmol) and ethyl 4-nitrobenzoylacetate (58 mg, 0.24 mmol) in ODCB (15 mL), DBU (0.12 mL, 0.81 mmol) was added dropwise. After 40 min, the mixture underwent column chromatography on silica gel, using cyclohexane to elute C_{60} and then cyclohexane–toluene 1 : 1 to elute compounds **9**[29] (8% yield, 13% based on recovered C_{60}) and **10**. 16% yield (25% based on recovered C_{60}); FTIR (KBr) ν 2920, 1747, 1702, 1526, 1343, 1265, 1230, 1205, 1183, 703, 578, 526 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.73 (d, 2H, J = 8.6 Hz), 8.50 (d, 2H, J = 8.6 Hz), 4.49 (q, 2H, J = 7.1 Hz), 1.32 (t, 3H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 183.38, 163.04, 150.69, 145.29, 145.08, 145.04, 144.97, 144.67, 144.55, 144.46, 144.26, 143.65, 143.54, 143.49, 142.82, 142.66, 141.94, 141.50, 140.94, 140.87, 140.09, 138.37, 137.16, 130.14, 124.10, 71.34, 63.48, 55.29, 29.82, 14.04; UV-vis ($CHCl_3$), λ_{max} 273, 326, 427, 489, 685; *m*/*z* (MALDI-TOF) 954 (M^+).

Conclusions

In this work we have synthesized three new fullerene-nitrobenzene derivatives (**5**, **8** and **10**) and their electrochemistry has been studied. The CPE of these compounds led to retro-Bingel processes, resulting in the formation of C_{60}. Furthermore, the formation of bis-adducts was observed. The structural and electronic differences between the compounds are reflected in the different extent of the retro-Bingel reaction. As anticipated, going from **5** to **10**, the amount of C_{60} obtained increases, as the addends become more "Bingel-like". The ESR signals of **5**, **8** and **10** during the different stages of the electrolysis showed how spin localization changed from fullerene to nitrobenzene-based and allowed the measurement of electronic effects induced by electron withdrawing substituents in the case of **10**. For this compound, an intermediate ESR spectrum has been simulated and assigned to a possible structure along the retro-Bingel pathway.

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References

1 C. Bingel, *Chem. Ber.*, 1993, **126**, 1957.

2 (*a*) D. M. Guldi, H. Hungerbühler and K.-D. Asmus, *J. Phys. Chem.*, 1995, **99**, 9380; (*b*) C. Boudon, J.-P. Gisselbrecht, M. Gross, L. Isaacs, H. L. Anderson, R. Faust and F. Diederich, *Helv. Chim. Acta*, 1995, **78**, 1334.

3 M. Keshavarz-K., B. Knight, R. C. Haddon and F. Wudl, *Tetrahedron*, 1996, **52**, 5149.

4 F. Cardullo, P. Seiler, L. Isaacs, J.-F. Nierengarten, R. F. Haldimann, F. Diederich, T. Mordasini-Denti, W. Thiel, C. Boudon, J.-P. Giesselbrecht and M. Gross, *Helv. Chim. Acta*, 1997, **80**, 343.

5 F. Arias, Y. Yang, L. Echegoyen, Q. Lu and S. R. Wilson, "Electrochemistry of Methanofullerenes and Methanofulleroids: Interconversion and Decompositions at Very Negative Potentials" in *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, Karl Kadish and Rodney Ruoff, Editors, The Electrochemical Society Proceedings Series 95-10, page 200, Pennington, NJ, 1995.

6 R. Kessinger, J. Crassous, A. Herrmann, M. Rüttimann, L. Echegoyen and F. Diederich, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1919.

7 C. Boudon, J.-P. Gisselbrecht, M. Gross, A. Herrmann, M. Rüttimann, J. Crassous, F. Cardullo, L. Echegoyen and F. Diederich, *J. Am. Chem. Soc.*, 1998, **120**, 8545.

8 C. Boudon, J.-P. Gisselbrecht, M. Gross, A. Herrmann, M. Rüttimann, J. Crassous, F. Cardullo, L. Echegoyen and F. Diederich, *J. Am. Chem. Soc.*, 1998, **120**, 7860.

9 J. Crassous, J. Rivera, N. S. Fender, L. Shu, L. Echegoyen, C. Thilgen, A. Herrmann and F. Diederich, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 1613.

10 (*a*) N. S. Fender, B. Nuber, D. I. Schuster, S. R. Wilson and L. Echegoyen, *J. Chem. Soc., Perkin Trans. 2*, 2000, 1924; (*b*) L. E. Echegoyen, F. D. Djojo, A. Hirsch and L. Echegoyen, *J. Org. Chem.*, 2000, **65**, 4994.

11 N. N. P. Moonen, C. Thilgen, L. Echegoyen and F. Diederich, *Chem. Commun.*, 2000, 335.

12 R. Kessinger, N. S. Fender, L. E. Echegoyen, C. Thilgen, L. Echegoyen and F. Diederich, *Chem. Eur. J.*, 2000, **6**, 2184.

13 (*a*) G. A. Burley, P. A. Keller, S. G. Pyne and G. E. Ball, *Chem. Commun.*, 2001, 563; (*b*) I. A. Nuretdinov, V. V. Yanilkin, V. P. Gubskaya, N. I. Maksimyuk and L. Sh. Berezhnaya, *Russ. Chem. Bull.*, 2000, **49**, 427.

14 M. W. J. Beulen, L. Echegoyen, J. A. Rivera, M. A. Herranz, A. Martín-Domenech and N. Martín, *Chem. Commun.*, 2000, 917.

15 M. W. J. Beulen, J. A. Rivera, M. A. Herranz, B. Illescas, N. Martín and L. Echegoyen, *J. Org. Chem.*, 2001, **66**, 4393.

16 M. W. J. Beulen, J. A. Rivera, M. A. Herranz, A. Martín-Domenech, N. Martín and L. Echegoyen, *Chem. Commun.*, 2001, 407.

17 (*a*) B. Knight, N. Martín, T. Ohno, E. Ortí, C. Rovira, J. Veciana, J. Vidal-Gancedo, P. Viruela, R. Viruela and F. Wudl, *J. Am. Chem. Soc.*, 1997, **119**, 9871; (*b*) T. Ohno, N. Martín, B. Knight, F. Wudl, T. Suzuki and H. Yu, *J. Org. Chem.*, 1996, **61**, 1306.

18 D. Y. Yang, O. Han and H. W. Liu, *J. Org. Chem.*, 1989, **54**, 5402.

19 W. E. Doering and C. H. De Puy, *J. Am. Chem. Soc.*, 1953, **75**, 5955.

20 M. Regitz, *Chem. Ber.*, 1965, **98**, 1210.

21 M. W. J. Beulen and L. Echegoyen, *Chem. Commun.*, 2000, 1065.

22 L. Echegoyen and L. E. Echegoyen, *Acc. Chem. Res.*, 1998, **31**, 593.

23 (*a*) V. Brezova, A. Stasko, P. Rapta, G. Domschke, A. Barti and L. Dunsch, *J. Phys. Chem.*, 1995, **99**, 16234; (*b*) M. Diekers, A. Hirsch, S. Pyo, J. Rivera and L. Echegoyen, *Eur. J. Org. Chem.*, 1998, 1111; (*c*) L. Shu, S. Pyo, J. Rivera and L. Echegoyen, *Inorg. Chim. Acta*, 1999, **292**, 34; (*d*) V. Brezova, A. Stasko, D. Dvoranova, K.-D. Asmus and D. M. Guldi, *Chem. Phys. Lett.*, 1999, **300**, 667; (*e*) T. Da Ros, M. Prato, D. M. Guldi, M. Ruzzi and L. Pasimeni, *Chem. Eur. J.*, 2001, **7**, 816.

24 (*a*) G. R. Stevenson, R. C. Recter, D. G. Ross and D. G. Frye, *J. Am. Chem. Soc.*, 1984, **88**, 1855; (*b*) G. R. Stevenson, *J. Phys. Chem.*, 1998, **92**, 493; (*c*) G. R. Stevenson and L. Echegoyen, *J. Phys. Chem.*, 1972, **76**, 1439; (*d*) S. K. Wang and J. K. S. Wan, *Can. J. Chem.*, 1973, **51**, 753.

25 A. H. Maki and D. H. Geske, *J. Am. Chem. Soc*, 1961, **83**, 1852.

26 (*a*) G. R. Stevenson and L. Echegoyen, *J. Phys. Chem.*, 1973, **77**, 2339; (*b*) G. R. Stevenson, L. Echegoyen and H. Hidalgo, *J. Phys. Chem.*, 1975, **79**, 152.

27 P. L. Boulas, Y. Zuo and L. Echegoyen, *Chem. Commun.*, 1996, 1547.

28 M. H. Hall, H. Lu and P. B. Shevlin, *J. Am. Chem. Soc.*, 2001, **123**, 1349.

29 Y. Wang, J. Cao, D. I. Schuster and S. R. Wilson, *Tetrahedron Lett.*, 1995, **36**, 6843.