Evidence for the Formation of Singly Bonded Dimers During the Reductive Electrochemistry of Methanofullerenes

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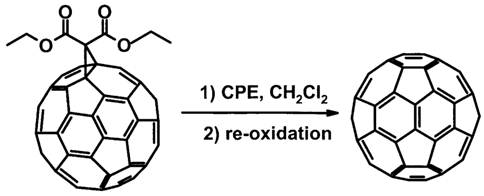
Abstract: Four methanofullerene derivatives, with phosphonate or sulfone groups attached to a C_{60} core through a Bingel procedure, were synthesized to probe their stability upon electrolytic reduction. Derivatives **1** and **2** are the most stable upon electroreduction and do not exhibit retro-cyclopropanation reactions until more than three electrons per C_{60} derivative are transferred. The cyclopropane ring is then removed and $C_{60}(>CH_2)_n$ ($n = 1-3$) products result from reactions of the trianion of C_{60} with the solvent, CH_2Cl_2. The situation with diphosphonate **3** or phosphonatecarboxylate **4** is dramatically different. For **3**, quantitative retro-cyclopropanation occurs when 2.8 e^- per molecule are transferred. In the case of **4**, when more than two electrons per molecule are transferred, there is evidence of the reversible formation of a very stable intermediate, which is oxidized at a potential 500 mV more positive than the first fullerene-based reduction of the parent compound. Electrolysis of a simple C_{70}-Bingel monoadduct (**5**) also exhibits the formation of a similar intermediate. On the basis of cyclic voltammetry, ESR spectroscopy, and MALDI analysis of products, the intermediate observed during the electrolysis of compounds **4** and **5** is assigned to a dimeric structure.

Keywords: cyclic voltammetry · dimerization · fullerenes · radical ions · retro-cyclopropanation

Introduction

The introduction and easy removal of protective groups in fullerene chemistry enables the design of structures that are otherwise not accessible by direct synthesis. Several convenient protection/deprotection schemes have been developed for fullerene derivative preparation,[1–6] one of which consists in a cyclopropanation/retro-cyclopropanation scheme introduced by us.[7–11] This methodology was developed following our observation of how controlled potential electrolysis (CPE) at the second reduction potential of diethyl 1,2-methano-[60]fullerene-61,61-dicarboxylate (see Scheme 1)[12] in CH_2Cl_2 led to >80% yields of recovered C_{60}. This reaction was called the retro-Bingel reaction, since it is the reverse of the well-known Bingel–Hirsch addition of malonate to form cyclopropane rings on fullerenes.[13] Soon after its discovery, this electrochemical retro-cyclopropanation reaction was successfully applied to a large number of Bingel derivatives of C_{60}, C_{70}, C_{76}, as well as C_{2v}- and D_3-C_{78}.[7–9, 12] Additionally, new isomers of C_{84} and a novel C_{78} bis-adduct were isolated using this methodology.[10, 11]



Scheme 1. Retro-Bingel reaction on C_{60}.

Some spiromethanofullerenes also exhibit electrochemical removal of the methano bridge to form C_{60} in high yields.[14] Wudl and co-workers described the electrochemical irreversibility of methanofullerenes bearing quinone type addends and proposed a mechanism presumably initiated by opening of the three-membered ring.[15] When these compounds were electroreduced in THF, efficient addend removal was also noticed, and a new reaction pathway was observed, namely, an electrochemically induced intermolecular adduct transfer. Such a reaction pathway in THF was not observed for the diethyl 1,2-methano[60]fullerene-61,61-dicarboxylate.[14b] Interestingly, the bis-adduct regioisomer distribution found after electrolysis of the mono-adduct in THF differs signifi-

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cantly from that obtained when the bis-adducts were prepared by following the usual synthetic route.[16] A possible mechanism was proposed to explain these results; this involved the formation of dimers in which two fullerene cages share one or two addends.[14b] Using digital simulations of the cyclic voltammetric results of these spiromethanofullerenes has afforded a better understanding of the mechanistic details involved in these electroreductive reactions.[17]

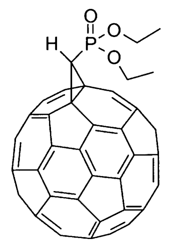
Although some effort has been devoted to try to understand the mechanism that governs these retro-cyclopropanation processes, no product characterization has been reported yet. Nuretdinov et al.[18] have published several papers in which they studied bis(diethoxycarbonyl) or bis(diethoxyphosphoryl) fullerene derivatives electrochemically and by ESR spectroscopy. They also observed that retro-cyclopropanation occurs, and on the basis of cyclic voltammetry and the rate constants derived from it, they proposed a mechanism involving the possibility of a dimerization process, but without proof.

Two articles relevant to the work presented here were published very recently. Konarev et al.[19] isolated a singly bonded $(C_{70}^{-})_2$ dimer formed during the preparation of a complex of hexamethoxycyclotriveratrylene with C_{70} fulleride. Independently, Komatsu et al.[20] synthesized a singly bonded C_{60} dimer by the reaction of C_{60}^{2-} with diethyl iodomethylphosphonate, followed by treatment with iodine.

In this article we report, for the first time, the observation and detection of intermediate species during the reductive retro-cyclopropanation reaction of a phosphonatecarboxylate Bingel derivative of [60]fullerene and of a bis(ethoxycarbonyl) derivative of methano[70]fullerene. Using electrochemistry, ESR spectroscopy, and product analysis we propose a dimerization mechanism during the reductive electrolysis of some fullerene derivatives.

Results and Discussion

Synthesis: The synthetic procedure for the preparation of methanofullerenes **1**–**4** is based on the Bingel reaction[13] of C_{60} with bromomethylene derivatives, which generate α-bromocarbanions in the presence of a base. Different pairs of base/solvent systems were tried. The best results were obtained when tetraethyl bromomethanediphosphonate,[21] ethyl 2-bromo-2-(diethoxyphosphoryl)acetate[22] or 1-bromoethyl-*p*-tolylsulfone[23] were prepared and treated with C_{60} in toluene or THF. The bases used were DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene), potassium *tert*-butoxide, or lithium bis(trimethylsilyl)amide (see Experimental Section for details). Few articles have been published concerning the synthesis of methanofullerene derivatives bearing phosphanyl or dialkoxyphosphoryl substituents,[24] and the latter seem to form similarly to ethoxycarbonylmethano derivatives. The present compounds were designed to probe the effects of slightly different electron-withdrawing abilities, different orbital distributions for delocalized negative charge, and different molecular size on the electroreductive retro-cyclopropanation reactions.



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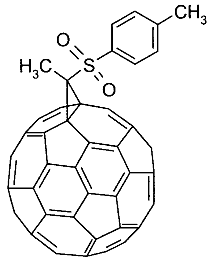

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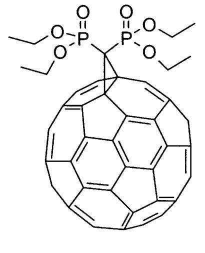

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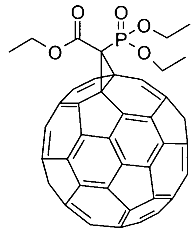

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The compounds were characterized by using different spectroscopic techniques. The FTIR spectra (KBr) of **1**, **3**, and **4** show two sharp, strong peaks at 1265 and 1016 cm^{-1}, corresponding to the vibration frequencies of P=O and P–O, respectively. Methanofullerenes **1**, **2**, and **4** have C_s symmetry and **3** has C_{2v} symmetry according to the ^{13}C NMR spectra. For **3**, 20 signals were observed, 16 of which are in the sp^2-hybridized fullerene region ($\delta = 146.1-140.3$ ppm), while similar fullerene resonances are seen for **1**, **2**, and **4**, some of which are overlapping. The coupling constants J_{HP} and J_{CP} were measured from the corresponding ^{1}H and ^{13}C NMR spectra, and the ^{31}P NMR spectra afforded the different shielding effects in the phosphonate series **1** ($\delta = 16.91$ ppm), **3** ($\delta = 15.14$ ppm) and **4** ($\delta = 11.92$ ppm). The [6–6] adduct structures of these compounds were confirmed by the observation of the characteristic band of dihydrofullerenes around 426 nm in the UV-visible spectra. Additionally, the HR-MALDI-TOF-MS spectra were consistent with the assigned structures.

Reductive electrochemistry of compounds 1–4: The electrochemical behavior of compounds **1**–**4** has been investigated by cyclic voltammetry in dichloromethane as shown in Figure 1 (see Supporting Information for detailed voltammetric data). Based on typical fullerene core reductions,[25] all of these compounds clearly exhibit three fullerene-based reductions designated as C_1, C_2, and C_3. We assume that the fourth reduction of compounds **3** and **4** (C_4) is based on the addend. It is well known that upon fullerene mono-addition loss of conjugation leads to a LUMO that is higher in energy and thus to a decreased electron affinity for derivatized fullerenes. In our case, the positive shifts (see Table 1) obtained for the first reduction step of C_{60} adducts **1**–**4**, when compared to the parent C_{60}, evidence the strong electron-withdrawing abilities of the substituent groups in the methano–carbon addend, following the order $SO_2Ph > COOEt > PO(OEt)_2$. These structures are representatives of the still rare group of fullerene derivatives that undergo reduction

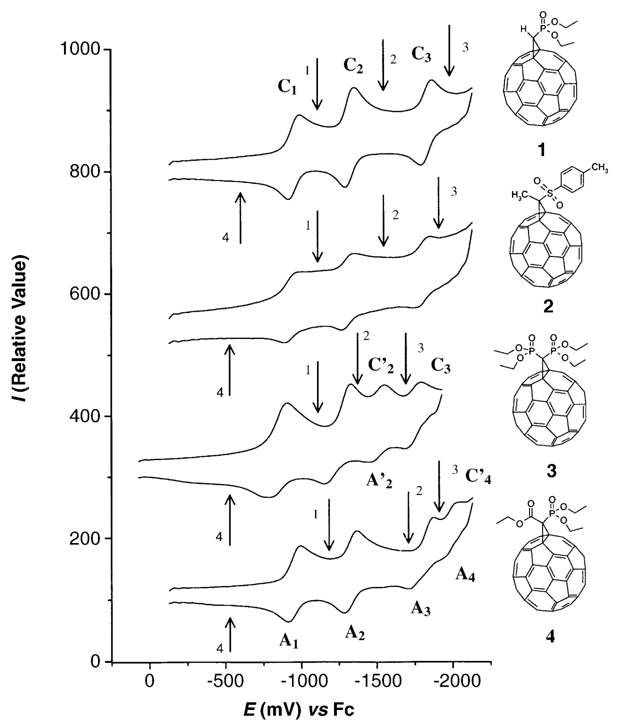


Figure 1. Cyclic voltammograms for 0.1 mM solutions of the methanofullerenes **1**–**4** in dichloromethane at $v = 100\,mV\,s^{-1}$. $TBAPF_6$ (0.1 M) was used as supporting electrolyte, GC as working electrode, Pt as counter electrode and an $Ag/AgNO_3$ electrode in a CH_3CN solution as quasi-reference electrode, $T = 25\,°C$.

Table 1. Redox potentials of **1**–**4** versus ferrocene in dichloromethane [mV].[a]

Compound	$E_{1/2}$ (C_1)	$(\Delta E)_1 = E_{1/2} - (E_{1/2})_{C60}$
C_{60}	– 980	–
1	– 960	20
2	– 933	47
3	– 941	39
4	– 938	42

[a] Electrochemical measurements were performed using a BAS 100 W Electrochemical Analyzer (Bioanalytical systems), GC working electrode, an Ag/Ag^+ pseudo-reference electrode and a Pt counter electrode, $TBAPF_6$ (0.1 M) was used as supporting electrolyte and the scan rate was $100\,mV\,s^{-1}$.

more easily than C_{60}.[26] Similar electrochemical behavior has been recently reported for compounds **3** and **4**.[18, 27]

Compounds **1** and **2** show an electrochemical behavior close to that exhibited by the parent C_{60}[25] on the cyclic voltammetric timescale. The fullerene derivatives are reduced in three reversible, monoelectronic, diffusion-controlled processes. These compounds were also subjected to bulk electrolyses in dichloromethane containing 0.1 M Bu_4NPF_6 under high-vacuum conditions. Bulk electrolyses were performed after each reduction step at a potential 100 to 150 mV more negative than the corresponding reduction peak potentials (arrows 1, 2, 3 in Figure 1).

For each of the first two reduction steps, bulk electrolyses confirmed that 1 e^- per C_{60} derivative molecule was transferred. Re-oxidation (arrow 4 in Figure 1) and purification of the products showed that the starting material was quantitatively recovered. These observations clearly prove that the anion and dianion are stable under these conditions. However, controlled potential electrolyses of **1** and **2** performed after the third reduction wave (arrow 3) resulted in a steady non-background current instead of the typical current exponential decay, indicating a subsequent chemical reaction during electrolysis (EC mechanism, heterogeneous electron-transfer reaction followed by homogeneous chemical reaction). Arbitrarily, the reduction was interrupted when 4 e^- per C_{60} adduct molecule were discharged. The cyclic voltammograms recorded after reduction and solution re-oxidation showed double waves assigned to the presence of two different fullerene derivatives in solution (see Supporting Information for graphs). After silica column purification, these products were assigned to starting compound **1** or **2** and methanofullerenes $C_{60}(>CH_2)_n$ (mainly $n = 2$) in a ratio 1:1, based on HPLC and MALDI mass spectrometry analyses. Such methanofullerene formations have been previously reported for the reaction of [60]fullerene trianions in dichloromethane.[28]

These results clearly demonstrate that compounds **1** and **2** are less prone to retro-cyclopropanation due to the reduced charge stabilization on the methano–carbon group relative to bis(ethoxycarbonyl)methano[60]fullerenes.[8b] Compounds **1** and **2** do not undergo retro-cyclopropanation reactions until the addition of more than three electrons, then the unstable trianionic state of C_{60} in dichloromethane reacts rapidly with the solvent to form methanofullerenes, $C_{60}(>CH_2)_n$.[28] This reaction can actually involve two main pathways: an electron transfer from a highly negative fullerene to CH_2Cl_2 and/or an S_N2 reaction between the nucleophilic fullerene and the solvent as reported by Kadish and co-workers for similar compounds.[29]

However, if the hydrogen atom attached to the methano carbon atom in compound **1** is substituted by another phosphonate group, as in compound **3**, or a carboxylate group, as in compound **4**, cyclopropane ring removal should become more favorable. Under cyclic voltammetric timescales, these C_{60} adducts exhibit irreversible reduction steps, presumably resulting from cleavage after reduction of one of the cyclopropane bonds connecting the addend to C_{60}. In the case of the diphosphonate C_{60} adduct **3**, the cyclic voltammogram shown in Figure 1 exhibits an irreversible chemical reaction following the second reduction wave C_2. Compound **3** exhibits a one-electron, reversible, diffusion-controlled, fullerene-based reduction (step C_1), followed by a bi-electronic irreversible step, as reported in a recent article.[27] This second step is dependent on the potential sweep, as other authors have observed.[18b] The third monoelectronic reduction wave (C_3) is fullerene-based, and is followed by a reduction wave probably due to the organic addend, which in fact is removed after reductive electrochemistry with the concurrent disappearance of the wave in the cyclic voltammogram (see Figure 2, solid line).

Controlled potential electrolysis of methanofullerene **3** after the first reduction wave (arrow 1, Figure 1) resulted in a discharge of 1 e^- per molecule and was fully reversible. Figure 2 presents the important voltammetric changes observed as the electrolysis proceeded. Cyclopropane ring removal occurred when bulk electrolysis was performed after

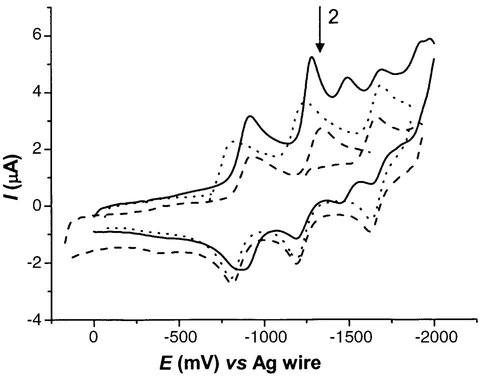


Figure 2. Bulk electrolysis for compound **3**. Cyclic voltammetric curves for a 0.1 mM CH_2Cl_2 solution of **3** at 100 mV s^{-1}, GC as working electrode, Pt-mesh as counter electrode and an Ag wire as a quasi-reference electrode, $T = 25$ °C, $TBAPF_6$ (0.1M) was used as supporting electrolyte. Solid line: electrochemical behavior before reduction. Dashed line: voltammogram after discharging 2.84 e^- per molecule. Dotted line: voltammogram after re-oxidation.

the second reduction wave (arrow 2 in Figures 1 and 2). At that potential, 2.84 e^- per fullerene monoadduct were discharged (dashed line). No starting compound **3** was present after electrolysis at C_3 and the cyclic voltammogram corresponds to that of the C_{60} dianion. C_{60} was recovered after oxidizing the solution mixture (dotted line). Product purification led to the quantitative recovery of C_{60} based on HPLC, UV-visible spectroscopy, and MALDI MS analyses. So, phosphonate groups behave as good electron-withdrawing groups when fullerene monoadducts are reduced as reported elsewhere.[18]

A similar retro-cyclopropanation reaction occurred for the disubstituted methanofullerene **4**. However, substitution of a phosphonate by a malonate group resulted in substantial differences during the course of the reductive electrolytic experiment.

On the cyclic voltammetric timescale, compound **4** exhibits four monoelectronic, diffusion-controlled reduction processes, see Figures 1 and 3. The reductions C_1, C_2, and C_3 are fullerene-based,[25] whereas C_4 is addend-based. For this compound, the chemical reaction that leads to cyclopropane ring removal occurs after the third reduction step on the CV timescale, since the corresponding wave presents a chemically irreversible behavior.

Controlled potential electrolyses, performed after each reduction step of **4**, showed that a chemical reaction occurred when more than 2 e^- per molecule were transferred. As for compounds **1**, **2**, and **3**, the first two electron reductions are fullerene-based and reversible, based on bulk re-oxidation and product analyses. Purification of the solution led to the quantitative recovery of the starting material. However, when the transferred charge corresponds to more than 2 e^- per fullerene adduct, unexpected changes in the cyclic voltammogram are observed. In Figure 3, the evolution of the electrochemical behavior of the solution is shown as the electrolysis proceeds. The original CV is shown as the solid line in Figure 3A. After 2.3 e^- per molecule were transferred, the CV shown as the dotted trace in Figure 3A was observed. Surprisingly and interestingly, the appearance of a new and reversible redox couple (A_0, C_0) approximately 0.5 V more positive than the first fullerene-based reduction is clearly observed in the voltammogram. Confirming this finding, controlled potential reduction showed a steady current related to a slow follow up chemical reaction instead of the typical current exponential decay observed until 2 e^- per compound were transferred. If reductive electrolysis is continued, when 2.75 e^- per molecule are transferred, the new redox couple is still present (Figure 3B, dashed line). After oxidation at this stage, the cyclic voltammogram depicted as the dotted line in Figure 3B is observed; this corresponds to that of C_{60}. Purification and analysis of the products shows a 57% yield of C_{60} and 33% of recovered starting material. On the other hand, if reductive electrochemistry of the intermediate is continued beyond 3 e^- per C_{60} monoadduct, efficient removal of the cyclopropane ring and formation of $C_{60}{}^{3-}$ occurs, which immediately reacts with the solvent. Methanofullerenes $C_{60}(>CH_2)_n$ ($n = 1-3$) have been quantitatively recovered after solution re-oxidation. Cyclic voltammograms recorded along the electrolytic sequence show that the dianion of compound **4** reacts to form the new intermediate, which then evolves to a mixture of the C_{60} dianion and the new intermediate, and finally to C_{60} upon oxidation. Therefore, the complete removal of the cyclopropane ring requires more than 3 e^- per fullerene derivative molecule and after 2 e^-, a new intermediate species forms during the electrolysis.

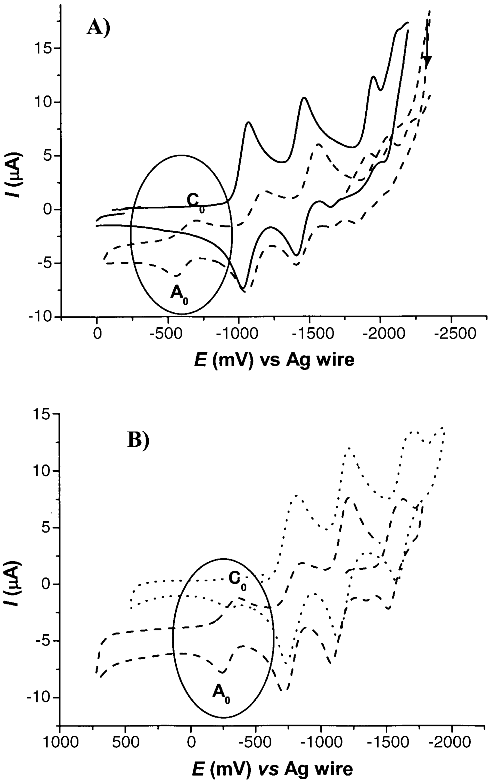


Figure 3. Controlled potential electrolysis results for **4**. Cyclic voltammetric curves for a 0.1 mM CH_2Cl_2 solution of **4** at 100 mV s^{-1}, GC as working electrode, Pt-mesh as counter electrode, and an Ag wire as a quasi-reference electrode, $T = 25$ °C, $TBAPF_6$ (0.1M) was used as supporting electrolyte. A) solid line: electrochemical behavior before reduction; dashed line: cyclic voltammogram after 2.3 e^- reduction. B) dashed line: cyclic voltammogram after 2.75 e^- reduction; dotted line: cyclic voltammogram after re-oxidation.

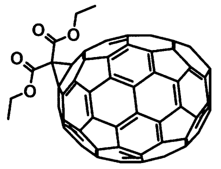
As previously noted, Komatsu et al.[20] recently reported the isolation of a dimer formed by coupling of monomer radicals with diethoxyphosphorylmethyl groups and they were able to obtain an X-ray crystal structure of it. Other dimeric fullerene derivatives have been generated in different ways[30] and similar observations to the ones obtained for **4**, oxidation of a fullerene derivative monoanion followed by a rapid recombination reaction to a neutral singly bonded dimer with 1-octynyl groups on each C_{60} cage, have been reported.[31]

The following brief consideration of our data, which clearly show the formation of a reversible and relatively stable intermediate, never observed previously, conclusively proves that dimerization is taking place. We postulate a dimerization reaction taking place in the electrolytic cell, from methanofullerene dianions, leading to the formation of negatively charged dimers. Oxidation or reduction of the solution leads to the disappearance of the intermediate dimer.

Retro-cyclopropanation reaction mechanism investigation—nature of the intermediate: During the course of this work, a relevant article was published by Konarev et al. in which a singly bonded C_{70} dimer was characterized by X-ray crystallography.[19] Based on these observations we reasoned that a C_{70} Bingel adduct might also exhibit similar electrochemical behavior to that of **4**, assuming that it could also form intermediate dimeric species. Indeed there were previous hints of such observations in our own work.[12] So we decided to explore in more detail the electroreductive processes occurring during electrolysis of a C_{70}-Bingel mono-adduct, paying particular attention to the potential formation of dimeric intermediates.

The electroreduction of **5** was monitored by cyclic voltammetry during controlled potential electrolysis under high-vacuum conditions by using our established protocol. As previously reported,[8b, 12] the C_{70}-Bingel adduct **5** shows chemical reversibility for the first and second reduction steps on the cyclic voltammetric timescale at $100\,\mathrm{mV\,s^{-1}}$. However, under bulk electrolysis conditions, irreversibility resulting from a retro-cyclopropanation reaction occurs when controlled potential electrolysis is carried out at the second reduction step after discharging 2 e^- per C_{70} adduct.[12]

Figure 4A shows that the starting material is electrochemically reduced sequentially by four mono-electronic reduction waves. We assume that C_1, C_2, and C_3 are fullerene-based and C_4 is adduct-based. When potentials are cathodically scanned beyond C_3 and C_4, an intermediate oxidation A_0 can be observed approximately 500 mV more positive than the first fullerene-based reduction C_1 (see Figure 4). This new oxidation is reversible, as shown by scanning a third segment immediately after A_0 giving rise to C_0. Interestingly, this intermediate is also observed when controlled potential electrolysis is carried out around the first reduction wave C_1 (see arrow 1 in Figure 4) when even fewer than 1 e^- per C_{70}-Bingel mono-adduct molecule is discharged. Cyclic voltammograms recorded at the end of such electrolysis (see Figure 4B) clearly shows that two species coexist in solution: the C_{70} adduct radical anion (A_1 oxidation) and the intermediate proposed (A_0 oxidation). Electrochemical oxidation of the solution leads to recovery of the starting material, whereas further reduction (potential fixed after C_2: arrow 2 in Figure 4) results in cyclopropane ring removal, that is, retro-cyclopropanation and C_{70} dianion formation. C_{70} and the starting fullerene derivative are recovered in a 3:1 ratio after re-oxidation of the solution following this second reduction, in accordance with our previous results.[8b]



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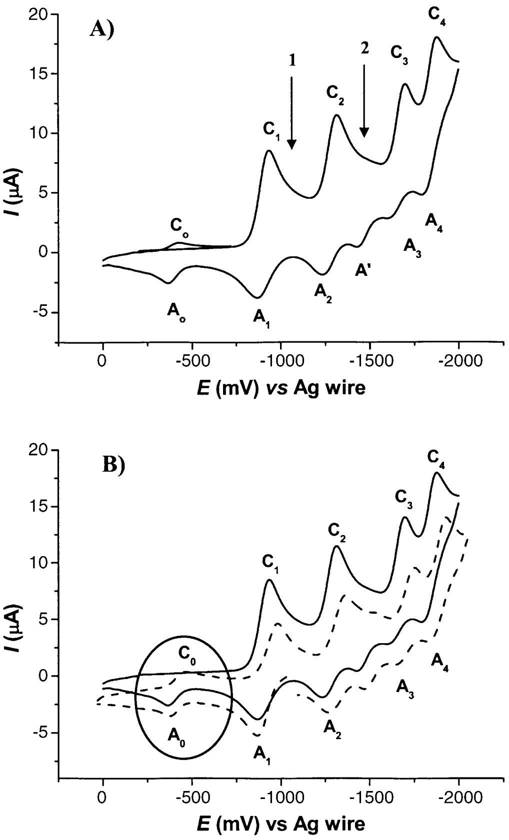


Figure 4. Reductive electrochemistry data for **5**. Cyclic voltammetric curves for a 0.1 mM CH_2Cl_2 solution of **5** at $100\,\mathrm{mV\,s^{-1}}$, GC as working electrode, Pt-mesh as counter electrode, and an Ag wire as a quasi-reference electrode, $T = 25\,^\circ C$, , $TBAPF_6$ (0.1M) was used as supporting electrolyte. A) cyclic voltammogram of **5**. B) Solid line: starting CV under high vacuum conditions; dashed line: cyclic voltammogram obtained after 1 e^- reduction of **5**.

We attribute this intermediate to a dimer containing two C_{70} adduct radical anions $[\{C_{70}C(COOEt)_2\}_2]^{2-}$. Figure 5A shows that for a fixed conversion of C_{70} mono-adduct by controlled potential electrolysis after the C_1 peak, increasing the starting compound concentration yields a larger relative dimer amount. This concentration dependence is in accord with the presence of the C_{70} adduct radical anions in equilibrium with their dimer. Moreover, the reduction product evolution during the first step of the electrolysis, presented in the Figure 5B, clearly shows that the C_{70} adduct radical anion

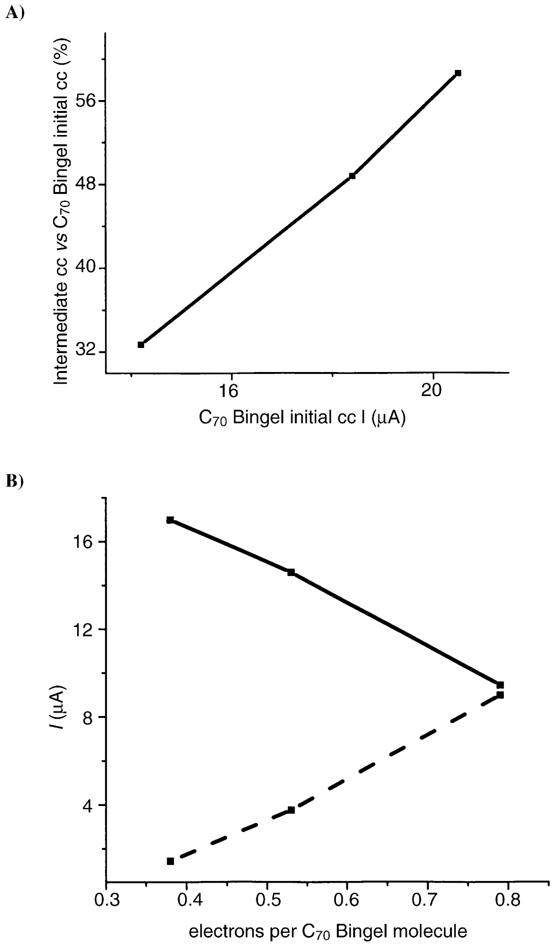
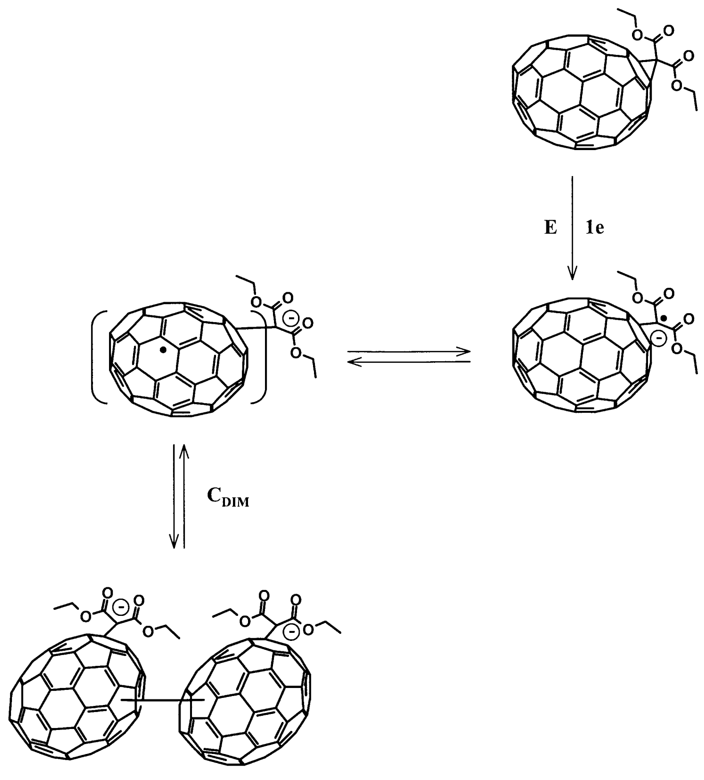


Figure 5. A) Concentration influence on intermediate structure formation, $n = 0.79$ e^- per C_{70} Bingel adduct. B) Reduction product evolution during C_{70}-Bingel adduct **5** reduction; solid line: C_{70}-monoadduct radical anion concentration, dashed line: intermediate derivative concentration. GC as working electrode, Pt-mesh counter electrode, and an Ag wire as a quasi-reference electrode, $T = 25\,^{\circ}C$.

concentration decreases, and that of the dimer increases, as more charge is transferred.

An increase in dimer concentration results in the adsorption of its oxidation product at the electrode, and C_0 then appears as a desorption peak. This last observation also favors the dimerization reaction, the dimer being less soluble in its neutral form (see Figure S6 in the Supporting Information).

To obtain additional information about the intermediates observed we recorded the ESR spectrum (see Supporting Information) of the electrolysis mixture under vacuum when less than 1 e^- per C_{70} adduct had been transferred. Two main signals were observed: one apparently fullerene-based signal with a $g = 1.99995$ and another with a $g = 2.00103$. These values are in reasonable agreement with the reported ionic complex of a singly bonded $(C_{70}^{-})_2$ dimer with cyclotriveratrylene[19] and other solid structures previously reported.[32] Solution EPR spectra of C_{70}^{-} have also been described in CH_2Cl_2[33], in THF, or THF/toluene (1:1) by chemical reduction with metallic potassium,[34] and, even when the conditions described are slightly different from the ones used here, there is close agreement with our data. No evident temperature effect on the dimerization equilibrium could be established from the small temperature range available in these experiments. Nevertheless, the ESR spectra appeared to be dimer concentration dependent. These observations are in agreement with the existence of an equilibrium between two C_{70} adduct radical anions if the negative charge is localized in the fullerene core or in the adduct. Therefore, we propose that during reductive electrolysis, a dimerization reaction occurs through an $EC_{DIM}E$ ($EC_{DIM}E$ = heterogeneous electron transfer, homogeneous chemical dimerization reaction, heterogeneous eletron transfer, in sequence) scheme, with preequilibration as presented in Scheme 2. Since the starting compound is primarily recovered after oxidation of the solution obtained after performing bulk electroreduction at C_1, the dimerization reaction must occur between two fullerene-based radicals, whereby negative charges are mainly localized on the addends. The malonate group plays an important role in the stabilization of the negatively charged dimer. Since the fullerene groups are essentially neutral in the dimer, its redox potential is shifted anodically. Several attempts to trap this intermediate for further analysis led to non-conclusive results, the intercage bond being too weak to resist out of vacuum conditions. However, controlled potential electrolysis of **5** (0.79 e^- per molecule) followed by quenching with an excess of CH_3I yielded a $m/z = 2081$ clear peak by MALDI mass spectrometry, consistent with dimer formation as postulated in Scheme 2, with the additional incorporation of two methyl groups, molecular oxygen, and sodium. Multiple experiments provided similar results with mass spectral peaks with m/z



Scheme 2. Proposed mechanism for the formation of dimeric [70]fullerene derivatives from electroreduced **5** (radical position and connecting bond between the C_{70} units are chosen arbitrarily with respect to possible regioisomers).

ratios that evidence the formation of dimeric [70]fullerene structures ($m/z > 1700$).

In Scheme 2, we propose a possible mechanism for the retro-Bingel reaction occurring in the C_{70}-Bingel derivative **5**. Cyclopropane ring opening happens as soon as the first electron is added. Reductive electrochemistry heterolytically opens the cyclopropane ring leading to charge formation either in the fullerene core or in the addends, and these interconvert at equilibrium. Dimers can then form between fullerene-based radicals, as represented in Scheme 2. On the cyclic voltammetric timescale, a fullerene-based oxidation (A_1) and an addend-based one (A_0) (see Figure 4) are observed for these equilibrium species. Bulk electro-oxidation leads to the recovery of the starting fullerene derivative and additional reduction results in the retro-Bingel reaction and the formation of the C_{70} dianion.

For the phosphonate adduct series (**1**, **3**, and **4**), it is reasonable to assume that similar pathways are involved in the reaction mechanism. The first two electrons are transferred primarily to the fullerene core in these compounds. At this point, three pathways can be followed depending on the electron-withdrawing affinity of the adduct. Mono-substituted methanofullerenes **1** and **2**, with poor ability to stabilize charge on the methano carbon atom, experience retro-cyclopropanation reactions only after the addition of more than 2 e^- per molecule. The $C_{60}(>CH_2)_n$ products are recovered after electron transfer or S_N2 reaction with the solvent. When the hydrogen is replaced by a phosphonate or a carboxylate group, the second electron addition opens the cyclopropane ring more or less completely, leading to a fullerene dianion diradical. The phosphonate groups do not seem to favor the formation of an anion diradical with delocalization of negative charge on the adduct. So, the addition of a third electron allows the complete removal of the addend and the quantitative recovery of the parent C_{60} after bulk electro-oxidation of the solution. However, the carboxylate group stabilizes the negative charge in the addend and a dimer can be formed when the transferred charge is between 2 and 3 e^- per C_{60} adduct derivative. In the electrolytic solution, a mixture of negatively charged starting material, dimer, and C_{60} dianion is then observed. On the cyclic voltammetric timescale, the corresponding characteristic oxidation peaks are A_0 (adduct based) and A_1 (fullerene based), respectively. Re-oxidation of the solution leads to the recovery of a mixture of C_{60} and the starting C_{60} derivative. Reduction of the dimer promotes the complete removal of the addend.

Conclusion

We have reported here the synthesis of four C_{60} methanofullerene derivatives with the purpose of analyzing their electrochemical behavior and understanding the pathways involved in the retrocyclopropanation reactions that they exhibit. Approximately 3 e^- per starting fullerene molecule are needed for cyclopropane ring removal. Analysis of the reductive electrochemistry of a classical C_{70}-Bingel derivative and a mixed phosphonatecarboxylate C_{60} adduct has provided evidence of a novel intermediate. This intermediate is stable and exhibits reversible electrochemical behavior. Based on a number of different electrochemical experiments, EPR spectroscopy, and MALDI mass spectrometry, the intermediates are assumed to be singly bonded dimeric structures between the fullerene cores. The electron-withdrawing affinity of the malonate group allows the stabilization of the negative charge in the adduct and then the formation of an intercage bond between two fullerene core radicals. Quantitative retro-cyclopropanation reactions can occur from the diphosphonate C_{60} derivative (**3**) without dimerization, whereas the mixed phosphonatemalonate C_{60} adduct (**4**) only yields a 60% of the parent C_{60}. Therefore, the dimerization reaction appears to act as an inhibiting pathway in the retro-cyclopropanation reaction mechanism.

Experimental Section

General methods: Reagents were purchased reagent grade from commercial suppliers and used without further purification. Toluene was distilled from Na and THF was distilled from Na/benzophenone ketyl. All reactions were carried out in standard, dry glassware under an inert atmosphere of Ar. Tetraethyl 1-bromomethane-1,1-diphosphonate,[21] ethyl 2-(diethoxyphosphoryl)acetate,[22] 1-[(1-bromoethyl)sulfonyl]-4-methylbenzene[27, 23] diethyl 3′*H*-cyclopropa[8,25](C_{70}-$D_{5h(6)}$)[5,6]fullerene-3′,3′-dicarboxylate[35] **5**[8b, 12, 13] were prepared according to literature procedures. TLC: Alugram SIL G/UV234, Macherey-Nagel, visualization by UV light at 254 or 366 nm. Column and flash chromatography: SiO_2 Merck 0.063 – 0.200 mesh or Al_2O_3, activity III. NMR spectra were recorded on Bruker AM-500 and Varian Gemini-300 or -200 in $CDCl_3$ unless otherwise stated. Infrared spectra (IR) were recorded on a Perkin – Elmer 1600-FTIR and reported in cm^{-1}, KBr pellets were used for all the measurements. UV/Vis spectra were recorded on a Varian Cary 5 spectrometer. FAB-MS: VG ZAB-2SEQ instrument, 3-nitrobenzyl alcohol (NOBA) as matrix; HR-MALDI-TOF-MS: Bruker Reflex spectrometer, matrix: 2,5-dihydroxybenzoic acid (DHB) or 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB).

Electrochemistry: Electrochemical measurements were performed by using a BAS 100 W electrochemical analyzer (Bioanalytical systems). An electrochemical cell designed to carry out CV and bulk electrolysis under high vacuum was used.[36] Fullerene mono-adducts **1**–**5** (2 – 5 mg) and supporting electrolyte, Bu_4NPF_6 (600 mg), were placed in the cell and degassed to 10^{-6} mmHg. The solvent, CH_2Cl_2 (12 mL), which had also been degassed, was then vapor-transferred into the cell, directly from CaH_2. Prior to CPE, cyclic voltammetry was performed with a glassy carbon working electrode to obtain the reduction potentials versus an Ag wire pseudo-reference electrode (note that upon electrolysis the pseudo-reference electrode may vary significantly; therefore, potential values should not be derived from these voltammograms). The latter was separated from the bulk solution using a vycor tip. Bulk electrolysis was carried out using Pt mesh electrodes for both working and counter electrode.

EPR experiments: The samples were analyzed using the X-band of a Bruker EMX spectrometer. In order to ensure that oxygen was not introduced in the system, the working electrode compartment in the bulk electrolysis cell was connected to a 3 mm o.d. pyrex tube.

Preparation of 3′-methyl-3′-[(4-methylphenyl)sulfonyl]-3′*H*-cyclopropa[1,9](C_{60}-I_h)[5,6]fullerene (2): A solution of lithium bis(trimethylsilyl)amide was prepared by addition, at room temperature, of *n*-BuLi/hexane (1.1 equiv) to a solution of bis(trimethylsilyl)amine (50 μL, 38 mg, 0.235 mmol) in THF (10 mL). At −78 °C a solution of 1-[(1-bromoethyl)sulfonyl]-4-methylbenzene (66 mg, 0.251 mmol) in THF was added, and the mixture was stirred at this temperature for 1 h. A solution of C_{60} (150 mg, 0.208 mmol) in 1,2-dichlorobenzene (10 mL) was added in such a way that the temperature stayed below −60 °C. The mixture was stirred at −40 °C for 2 h, then at room temperature for 14 h. The reaction was quenched by addition of brine (10 mL) and the mixture extracted several times with toluene. The combined organic layers were dried over Na_2SO_4 and evaporated in vacuo. Flash chromatography (SiO_2, toluene/pentane 90:10 → 100:0) afforded a mixture of **2** and C_{60}. Final purification by column chromatography (Al_2O_3, toluene/pentane 90:10) yielded pure **2** (5 mg, 2.6 %). $R_f = 0.66$ (SiO_2, toluene); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 8.17$ (d, $J = 8.4$ Hz, 2H), 7.54 (d, $J = 8.4$ Hz, 2H), 2.55 (s, 3H), 2.48 ppm (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 146.13$, 145.92, 145.32, 145.30, 145.27, 145.15, 144.94, 144.84, 144.79, 144.76, 144.75, 144.58, 144.48, 144.41, 144.06, 143.64, 143.54, 143.20, 143.13, 143.10, 143.07, 142.83, 142.35, 142.19, 142.08, 141.62, 141.51, 140.99, 140.84, 137.91, 135.14, 130.33, 129.49, 129.03, 128.22, 74.49, 57.13, 21.85, 16.00 ppm; IR (KBr): $\tilde{\nu} = 2955$ (s), 2911 (s), 2844 (s), 1422 (s), 1394 (s), 1374 (s), 1327 (s), 1261 (s), 1211 (s), 1183 (s), 1155 (s), 1101 (s), 1077 (s), 1033 (s), 967 (s), 838 (s), 811 (s), 750 (s), 716 (s), 688 (s), 666 (s), 594 (s), 572 (s), 544 (s), 522 cm^{-1} (s); UV/Vis ($CHCl_3$): λ_{max} (ε) = 324 (36021), 426 nm (4588.8 $L\,mol^{-1}\,cm^{-1}$); FAB-MS: m/z: 901.3 $[M]^+$, 720 $[C_{60}]^+$; MALDI-TOF HRMS $[M]^-$: m/z calcd for $C_{69}H_{10}O_2S$: 902.040; found: 902.041.

Preparation of diethyl 3′*H*-cyclopropa[1,9](C_{60}-I_h)[5,6]fullerene-3′-phosphonate (1) and tetraethyl 3′*H*-cyclopropa[1,9](C_{60}-I_h)[5,6]fullerene-3′,3′-diphosphonate (3): Tetraethyl bromomethanediphosphonate (30 mg, 0.082 mmol) was added to a solution of potassium *tert*-butanolate (10 mg, 0.089 mmol) in THF (5 mL) at −20 °C, and the solution was stirred for 30 min. A solution of C_{60} (50 mg, 0.69 mmol) in toluene (80 mL) was added at −40 °C. The mixture was allowed to warm up to room temperature and stirring was continued for 14 h. The reaction was quenched by addition of brine (10 mL), and the mixture extracted several times with toluene. The combined organic layers were dried over Na_2SO_4 and evaporated in vacuo. Column chromatography (Al_2O_3, toluene/AcOEt 95:5 → toluene/AcOEt 80:20) afforded **1** (21 mg, 35 %) and **3** (25 mg, 36 %).

Fullerene 1: $R_f = 0.63$ (SiO_2, toluene/AcOEt 60:40); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 4.52$ (quint, $J_{HH} = 7.1$ Hz, $^{3}J_{HP} = 7.1$ Hz, 4H), 4.22 (d, $^{2}J_{HP} = 4.5$ Hz, 1H), 1.59 ppm (t, $J_{HH} = 7.1$ Hz, 6H); ^{13}C NMR ($CDCl_3$, 125.7 MHz): $\delta = 149.28$, 149.25, 146.42, 146.37, 145.56, 145.21, 145.19, 145.12, 145.05, 144.70, 144.64, 144.63, 144.62, 144.55, 144.49, 144.34, 143.90, 143.66, 143.23, 143.02, 142.93, 142.88, 142.72, 142.37, 142.14, 142.08, 142.01, 140.99, 140.79, 140.42, 136.05, 68.93 (d, $^{2}J_{CP} = 4.9$ Hz), 63.42 (d, $^{2}J_{CP} = 6.2$ Hz), 33.33 (d, $^{1}J_{CP} = 185.5$ Hz), 16.69 ppm (d, $^{3}J_{CP} = 5.8$ Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): $\delta = 16.91$ ppm; IR (KBr): $\tilde{\nu} = 2977$ (s), 2922 (s), 1422 (s), 1389 (s), 1367 (s), 1256 (s), 1183 (s), 1161 (s), 1017 (s), 828 (s), 794 (s), 733 (s), 700 (s), 672 (s), 567 (s), 522 cm^{-1} (s); UV/Vis ($CHCl_3$): λ_{max} (ε) = 500 (2630), 427 (2830), 326 (22646), 256 nm (77083 $L\,mol^{-1}\,cm^{-1}$); FAB-MS: m/z: 871.7 $[M]^+$, 720.8 $[C_{60}]^+$; MALDI-TOF HRMS $[M]^-$: m/z calcd for $C_{65}H_{11}O_3P$: 870.0445; found: 870.045.

Fullerene 3: $R_f = 0.34$ (SiO_2, toluene/AcOEt 60:40); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 4.48$ (quint, $J_{HH} = 7.1$ Hz, $^{3}J_{HP} = 7.1$ Hz, 8H), 1.53 ppm (t, $J_{HH} = 7.1$ Hz, 12H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 146.12$, 146.08, 146.04 (t, $^{3}J_{CP} = 5.2$ Hz), 145.33, 145.17, 145.08, 144.96, 144.89, 144.70, 144.65, 144.06, 143.07, 143.01, 142.92, 142.35, 142.24, 140.98, 140.34, 68.20 (t, $^{2}J_{CP} = 4.1$ Hz), 63.91 (t, $^{2}J_{CP} = 3.1$ Hz), 39.84 (t, $^{1}J_{CP} = 153.8$ Hz), 16.61 ppm (t, $^{3}J_{CP} = 2.9$ Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): $\delta = 15.14$ ppm; IR (KBr): $\tilde{\nu} = 2977$ (s), 2922 (s), 2911 (s), 2855 (s), 1427 (s), 1383 (s), 1361 (s), 1255.6 (s), 1183 (s), 1155.6 (s), 1094 (s), 1050 (s), 1016 (s), 977 (s), 905 (s), 833 (s), 800 (s), 766.4 (s), 740 (s), 700 (s), 666 (s), 600 (s), 566 (s), 538 (s), 522 cm^{-1} (s); UV/Vis ($CHCl_3$): λ_{max} (ε) = 692 (1436), 487 (3617), 426 (5130), 325 nm (61412 $L\,mol^{-1}\,cm^{-1}$); MALDI-TOF-MS: m/z: 1029 $[M+Na]^+$, 927, 815, 745, 734, 720 $[C_{60}]^+$; MALDI-TOF HRMS $[M+Na]^+$: m/z calcd for $C_{69}H_{20}NaO_6P_2$: 1029.063; found: 1029.062.

Preparation of ethyl 3′-diethoxyphosphoryl-3′*H*-cyclopropa[1,9](C_{60}-I_h)[5,6]fullerene-3′-carboxylate (4): Ethyl 2-bromo-2-(diethoxyphosphoryl)acetate (101 mg, 0.333 mmol) and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) (50 µL, 51 mg, 0.335 mmol) was added to a solution of C_{60} (200 mg, 0.278 mmol) in toluene (150 mL). The mixture was sonicated in a water/ice bath for 4 h, after which time the reaction was quenched by addition of 1 M aq. HCl (20 mL) and the mixture extracted with toluene and CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and evaporated in vacuo. Column chromatography (Al_2O_3, toluene/CH_2Cl_2 50:50 → toluene/CH_2Cl_2 70:30) afforded **4** (76 mg, 29 %). ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 4.57$–4.53 (m, $J_{HH} = 7.1$ Hz, $^{3}J_{HP} = 7.1$ Hz, 6H), 1.55 (t, $J_{HH} = 7.1$ Hz, 6H), 1.46 ppm (t, $J_{HH} = 7.1$ Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 164.11$, 145.36, 145.27, 145.25, 145.14, 145.08, 145.02, 144.92, 144.87, 144.72, 144.65, 144.60, 144.57, 144.54, 143.98, 143.82, 143.14, 143.08, 142.97, 142.96, 142.70, 142.20, 142.16, 142.06, 141.88, 140.87, 140.84, 140.82, 136.93, 70.40 (d, $^{2}J_{CP} = 3.9$ Hz), 64.5 (d, $^{2}J_{CP} = 6.1$ Hz), 63.38, 49.05 (d, $^{1}J_{CP} = 163.6$ Hz), 16.55 (d, $^{3}J_{CP} = 6.0$ Hz), 14.27 ppm; ^{31}P NMR ($CDCl_3$, 121.5 MHz): $\delta = 11.92$ ppm; IR (KBr): $\tilde{\nu} = 2977$ (s), 2922 (s), 2844 (s), 1727 (s), 1461 (s), 1422 (s), 1383 (s), 1381 (s), 1261 (s), 1222 (s), 1177 (s), 1161 (s), 1094 (s), 1039 (s), 1016 (s), 978 (s), 794 (s), 740 (s), 700 (s), 672 (s), 600 (s), 588 (s), 572 (s), 522 cm^{-1} (s); UV/Vis ($CHCl_3$): λ_{max} (ε) = 494 (4337), 426 (5617), 326 nm (62416 $L\,mol^{-1}\,cm^{-1}$); FAB-MS: m/z: 942.4 $[M]^+$, 720 $[C_{60}]^+$; MALDI-TOF HRMS $[M]^-$: m/z calcd for $C_{68}H_{15}O_5P$: 942.0657; found: 942.066.

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