Selective Electrolytic Removal of Bis(alkoxycarbonyl)methano Addends from C_{60} Bis-adducts and Electrochemical Stability of C_{70} Derivatives

Roland Kessinger,[a] Nicolette S. Fender,[b] Lourdes E. Echegoyen,[b] Carlo Thilgen,[a] Luis Echegoyen,*[b] and François Diederich*[a]

Abstract: The novel mixed bis-adducts of C_{60}, (±)-**4**–(±)-**8** and **9**, with a bis(ethoxycarbonyl)methano addend (Bingel addend) and a second addend ([1,2]benzeno, but[2]eno, methaniminomethano, or diarylmethano) bridging 6,6-closed bonds of the carbon sphere were synthesized in two-step reactions. Each bis-adduct was exhaustively electrolyzed at the potential of the second fullerene-centered reduction step, resulting in the selective removal of the Bingel addend (retro-Bingel reaction) to produce the corresponding mono-adducts, which were isolated in yields of over 60%. These results open up the possibility of using the Bingel addend as a temporary protecting and directing group in the construction of multiple adducts of C_{60} with unusual addition patterns. The Bingel-type mono-adduct of C_{70} **10** and the constitutionally isomeric bis-adducts **11**, (±)-**12**, and (±)-**13** were also included in this investigation. A large difference in the electrochemical behavior between C_{70} bis-adducts and the corresponding C_{60} derivatives was observed. Thus, the intramolecular "walk-on-the-sphere" isomerization which occurs readily with Bingel-type bis-adducts of C_{60} under the conditions of two-electron controlled potential electrolysis (CPE) is only a minor reaction pathway in the series of C_{70} derivatives. The latter preferentially undergo retro-Bingel reaction.

Keywords: electrochemistry · electrolysis · fullerenes · protecting groups · retro-Bingel reaction.

Introduction

Among the various protocols developed for the covalent functionalization of fullerenes,[1–5] the Bingel reaction[6] and the azomethine ylide dipolar cycloaddition[7] are the most widely used methods. The original Bingel reaction and its modifications[8–10] generally proceed in good yield, and the bis(alkoxycarbonyl)methano addends (Bingel addends) introduced at 6,6-bonds of the carbon spheres are of high thermal and chemical stability. The macrocyclization of the carbon sphere by double Bingel addition of tethered bismalonates represents a highly effective method for precisely positioning organic chromophores such as crown ethers and porphyrins in close proximity to the fullerene surface, thus offering the potential for inducing profound changes in the properties of the molecular carbon allotrope.[11] The Bingel reaction has also been heavily applied in supramolecular construction involving fullerene components.[12]

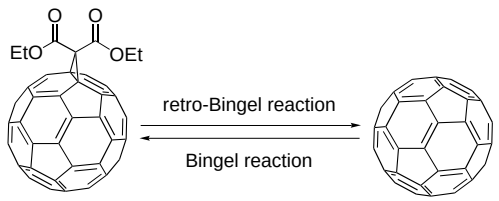
Regioselective multiple functionalization of fullerenes often requires the temporary introduction of an addend which protects reactive bonds, directs new incoming addends into specific positions, and after completion of these tasks, can be readily removed. Three protocols have been mainly applied in the past for this purpose. The first one consists of Diels–Alder additions of 9,10-dimethylanthracene, which are thermally readily reversible.[13] The second one is an elegant multistep protocol which was developed for the removal of the more stable cyclohexene rings fused to the carbon sphere by Diels–Alder addition with buta-1,3-dienes.[14, 15] The third method consists of the fusion of isoxazoline rings to the fullerene by dipolar cycloaddition with nitrile oxides and removal of the addend with $[Mo(CO)_6]$ or diisobutylaluminum hydride (DIBAL-H).[16]

During investigations of the electrochemical stability of anions of bis(ethoxycarbonyl)methano-functionalized fullerenes such as **1**,[17] we discovered that this addend can be electrochemically removed in high yield by exhaustive electrolytic reduction at constant potential.[18] We named this novel procedure the retro-Bingel reaction (Scheme 1).[19] A

[a] Prof. Dr. F. Diederich, Dipl.-Chem. R. Kessinger, Dr. C. Thilgen
Laboratorium für Organische Chemie
ETH-Zentrum
Universitätstrasse 16, 8092 Zürich (Switzerland)
Fax: (+41) 1-632-1109
E-mail: diederich@org.chem.ethz.ch

[b] Prof. Dr. L. Echegoyen, Dr. N. S. Fender, Dr. L. E. Echegoyen
Department of Chemistry
University of Miami
Coral Gables, FL 33124 (USA)
Fax: (+1) 305-284-4571
E-mail: echegoyen@miami.edu

  0947-6539/00/0612-2184 $ 17.50+.50/0

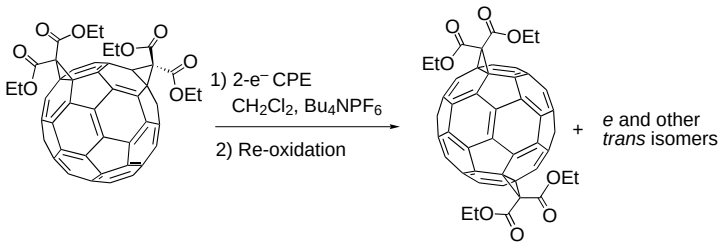


1

Scheme 1. The Bingel and retro-Bingel reactions.

first major application of the Bingel-retro-Bingel strategy was the preparation of pure constitutional isomers of higher fullerenes, such as C_{2v}-C_{78}[17c] and a new C_{84} isomer,[20] and, gratifyingly, of enantiomerically pure chiral higher fullerenes such as ^{f}C- and ^{f}A-C_{76}[18] and ^{f}C- and ^{f}A-C_{84}.[20]

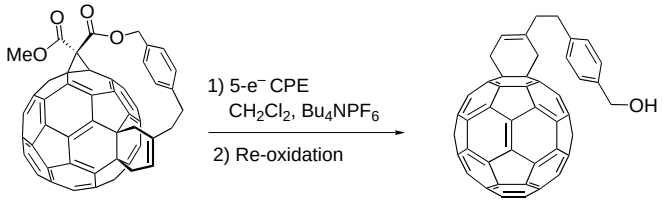
While investigating the retro-Bingel reaction, we also discovered an isomerization reaction, the "walk-on-the-sphere" rearrangement, where two bis(ethoxycarbonyl)-methano addends intramolecularly change their positions on the C_{60} sphere.[21] This rearrangement occurs when the electrolytic reduction is interrupted after only two electron-equivalents have been transferred (Scheme 2).



cis-3 *trans-2*

Scheme 2. The intramolecular "walk-on-the-sphere" rearrangement observed during two-electron controlled potential electrolysis (CPE).

Preliminary electrochemical investigations with the mixed bis-adduct **2** obtained by tether-directed remote functionalization[22] suggested that the chemoselective electrochemical removal of a Bingel addend from the fullerene sphere in the presence of a different addend might be possible (Scheme 3).[23] The reaction was very sluggish, and only traces

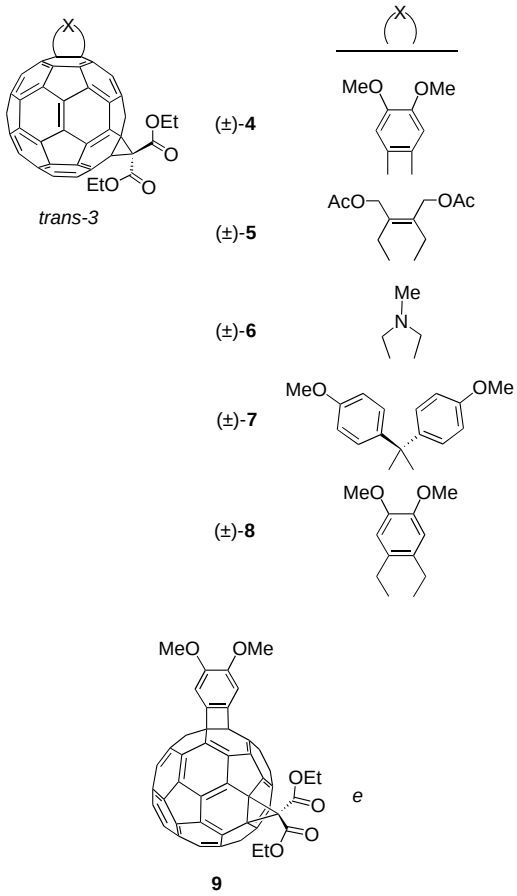


2 **3**

Scheme 3. First observation of the electrochemical retro-Bingel reaction of a mixed bis-adduct.[23]

of benzyl alcohol **3** could be isolated. Whereas the unambiguous identification of the product was impossible due to low yield and difficult workup, its UV/Vis spectrum clearly showed the characteristic bands around 435 and 700 nm of a Diels–Alder mono-adduct.[24]

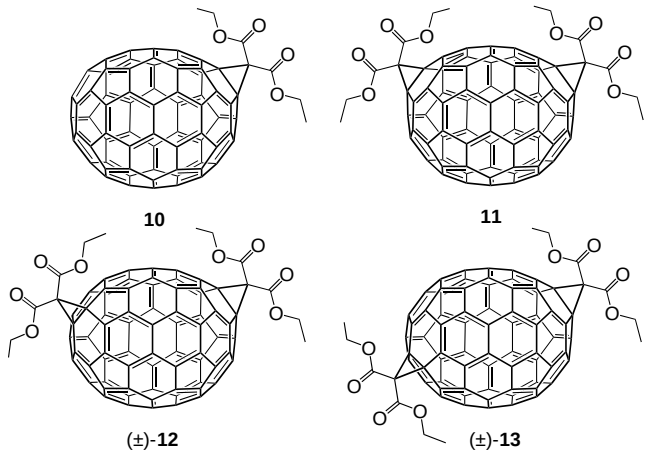
Inspired by these preliminary results, we undertook a more comprehensive investigation of the synthetic scope of the electrochemical retro-Bingel reaction and the possible use of the Bingel addend as a protecting and directing group. For this purpose, a series of mixed C_{60} bis-adducts (±)-**4**–(±)-**8** and **9** were synthesized and subjected to the electrochemical retro-Bingel reaction. In addition, we report here investigations on



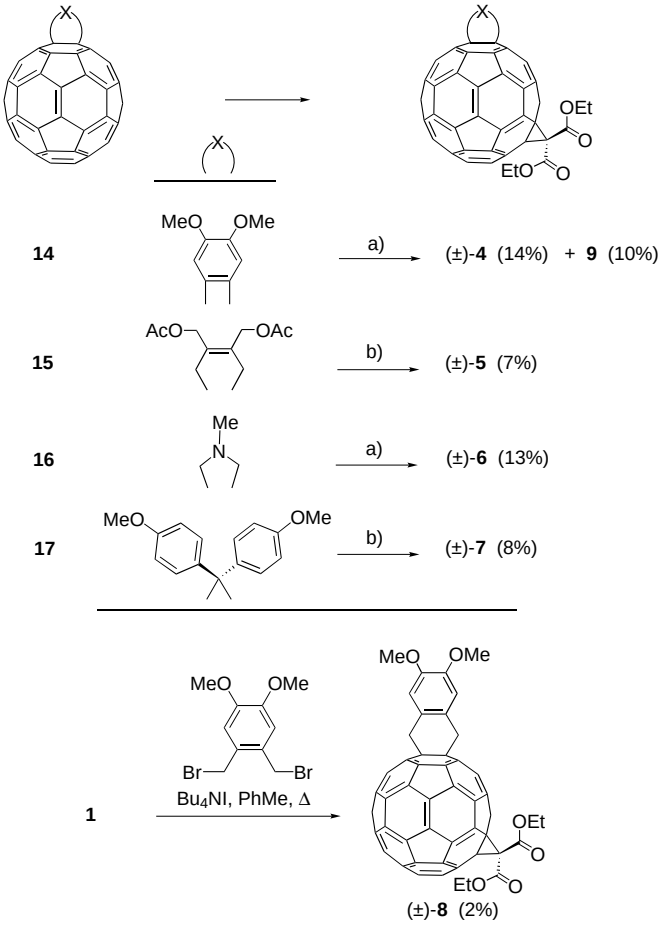
the retro-Bingel reaction and "walk-on-the-sphere" rearrangement of the C_{70} mono-adduct **10** and the three constitutionally isomeric bis-adducts **11**, (±)-**12**, and (±)-**13**, and compare the results with those obtained for analogous derivatives of C_{60}.

Results and Discussion

Synthesis: The C_{70} mono-adduct **10**[6a] and the constitutionally isomeric bis-adducts **11**, (±)-**12**, and (±)-**13**[6b, 25] were prepared as previously reported. Starting from the known C_{60} derivatives **14**,[26] **15**,[27] **16**,[28] and **17**,[29] respectively, the mixed *trans-3* bis-adducts (±)-**4**, (±)-**5**, (±)-**6**, and (±)-**7** were obtained by Bingel cyclopropanation and isolated in 7–



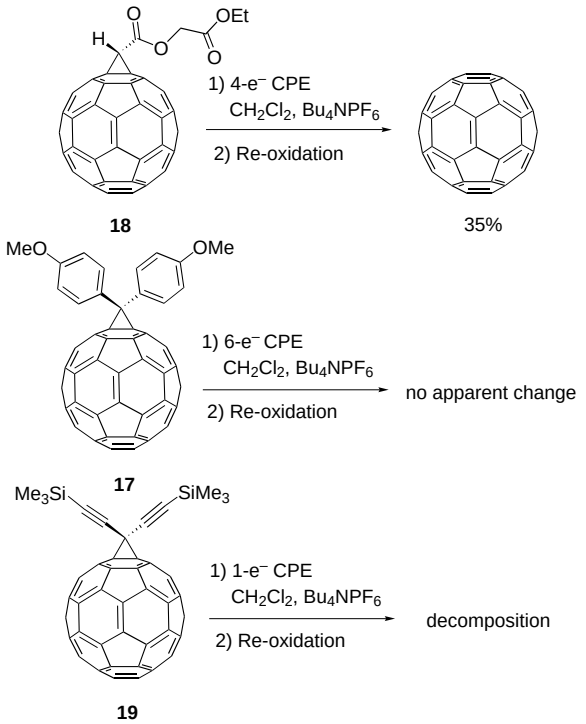
14% yield after extremely tedious column chromatographic separation from the other regioisomers formed (Scheme 4). Since the "walk-on-the-sphere" rearrangement of bis(alkoxycarbonyl)methano addends in C_{60} derivatives leads to a scrambling of the regioisomers during the retro-Bingel reaction,[21] the scope of the latter reaction can be fully investigated starting from only one of the possible[30] regioisomeric bis-adducts. Only in the Bingel cyclopropanation of **14** could the *e* isomer **9** be isolated in pure form (10% yield) by simple column chromatography. Among the two possible *e* isomers,[22] **9** was isolated exclusively according to ^{1}H and ^{13}C NMR spectroscopy. Bis-adduct (±)-**8** was obtained by Diels–Alder addition to **1** following a previously described[24] protocol. The low yield of 2% in this reaction is due to extreme difficulties in the isolation of the pure isomer and not due to an inherently problematic synthetic pathway. For analytical purposes and full characterization, all bis-adducts were completely purified by preparative HPLC (high performance liquid chromatography).[30] The *trans-3* isomers used in the preparative electrochemical experiments contained small amounts of other regioisomers (*trans-2*, *trans-4*, *e*; a total of less than 10%) which did not change the outcome of the retro-Bingel reactions in view of the above-mentioned scrambling of the regioisomers by the "walk-on-the-sphere" rearrangement.



Scheme 4. Synthesis of the mixed C_{60} bis-adducts. a) $EtO_2CCH_2CO_2Et$, I_2, DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), PhMe/CH_2Cl_2; b) $EtO_2CCHBrCO_2Et$, DBU, PhMe.

Electrochemical investigations of C_{60} derivatives: All experiments were performed using a home-made cell as previously described.[31] Constant potential electrolysis (CPE) was carried out under high vacuum in CH_2Cl_2 with Bu_4NPF_6 (0.1M) as supporting electrolyte (see Experimental Section for details). To determine the potential to be applied, the cyclic voltammograms (CV) of the compounds were recorded. The applied potential for CPE was typically chosen 100 mV more negative than the second reduction peak potential. After electrolysis, the solutions were exhaustively re-oxidized at 0 V before product analysis.

The retro-Bingel reaction occurs at the second reduction potential of bis(ethoxycarbonyl)methano[60]fullerenes. In the case of **18**[32] (Scheme 5), with only one carboxylic group



Scheme 5. Experiments demonstrating that efficient retro-Bingel reactions require two electron-withdrawing groups at the methano bridge.

0947-6539/00/0612-2186 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 12

directly attached to the cyclopropane ring, the dianion is stable under bulk electrolysis conditions. However, when electrolyzed at the third reduction potential, cleavage of the methano bridge is induced. In this case, the yield of the parent fullerene, C_{60}, drops remarkably (35%) compared to the yield obtained in the electrolysis of **1** (Scheme 1), which is typically higher than 80%.[18] Electrochemical cleavage of the cyclopropane ring also occurs when two cyano[19c] groups are attached. Thus, the presence of two strongly electron-withdrawing groups (EWG) attached to the cyclopropane ring is apparently necessary for efficient electrolytic removal of the addend.

In order to further test this hypothesis, mono-adducts **17** and **19**[33] were submitted to the conditions of the retro-Bingel reaction. In the case of **17**, which lacks electron-withdrawing groups at the methano bridge, it is not possible to cleave the cyclopropane ring electrochemically within the limits of the potential window of the solvent. Mono-adduct **19**, with two weakly electron-withdrawing (trimethylsilyl)ethynyl groups attached to the methano bridge, decomposes to an insoluble solid after reduction to the mono-anion. This decomposition is faster than a possible cyclopropane ring cleavage, and indeed, no C_{60} was detected in the reaction mixture after re-oxidation.

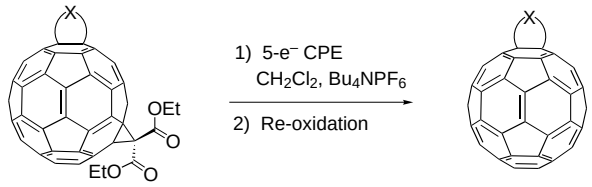
To demonstrate the stability in the reduced state of the other C_{60} mono-adducts (which lack Bingel addends), compounds **14**–**16** were subjected to CPE up to at least the trianionic stage. Upon re-oxidation to the neutral state, only starting material was present, confirming their stability.

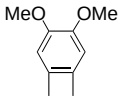
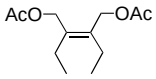
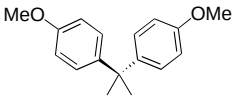
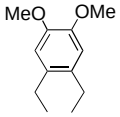
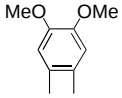
Having established that the mono-adducts **14**–**17** are stable under the electrochemical conditions of the retro-Bingel reaction, we turned our attention to the selective removal of a Bingel addend from fullerenes in the presence of other addends. Thus, the five *trans-3* bis-adducts (±)-**4**–(±)-**8** were subjected to the retro-Bingel reaction. The electrochemical reaction to the corresponding mono-adducts **14**–**17** and **20**[24] proceeded in most cases with yields over 60% (Table 1). These yields are encouraging for the use of the Bingel addend as a temporary protecting and directing group in fullerene chemistry, since two of the most commonly used addends, fused pyrrolidine[7, 34] and cyclohexene rings[35, 36] are perfectly stable under the conditions of the retro-Bingel reaction.

To study the effect of the retro-Bingel reaction on different regioisomers, the *trans-3* and *e* derivatives (±)-**4** and **9** were electrolyzed under similar conditions. The difference in their electrochemical behavior is only marginal, and the yield of mono-adduct **14** is practically the same in both conversions, considering the possible errors introduced during the manipulation of the small quantities of compounds used for the electrolysis experiments (2–3 mg). In view of the scrambling caused by the "walk-on-the-sphere" rearrangement during electrolysis, it is reasonable to assume that the same results may be obtained for the regioisomers of all the other compounds investigated here.

Throughout our studies of the retro-Bingel reaction, the cleaved addend has never been recovered due to its difficult separation from the electrolyte material. However, its recovery and characterization could be crucial in establishing the mechanism of the reaction. For this reason, (±)-**21** was synthesized by the Bingel macrocyclization reaction between

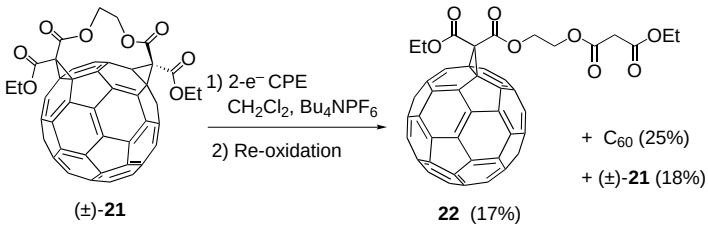
Table 1. Selective removal of bis(ethoxycarbonyl)methano addends in mixed C_{60} bis-adducts by the retro-Bingel reaction.



	X	
(±)-**4**		**14** (67%)
(±)-**5**		**15** (43%)
(±)-**6**		**16** (63%)
(±)-**7**		**17** (60%)
(±)-**8**		**20** (61%)
9 (*e* isomer)		**14** (65%)

C_{60} and 1,1′-(ethane-1,2-diyl) 3,3′-diethyl bis(malonate) and electrolyzed non-exhaustively at the second reduction potential. The electrolysis was stopped after 2.5 electrons per molecule were transferred. After exhaustive re-oxidation at 0 V, the mixture obtained was separated by column chromatography. Analysis of the isolated material showed that in addition to recovering some of the starting material, both C_{60} and **22** were also produced (Scheme 6). This is a clear indication that the leaving malonate remains intact during the cleavage of the cyclopropane ring.

Electrochemical investigations of C_{70} derivatives: The C_{70} mono-adduct **10**, similar to the C_{60} analogue **1**, shows chemical

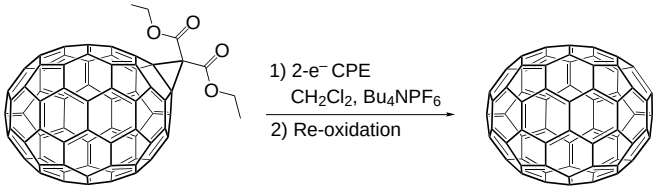


(±)-**21** **22** (17%)

Scheme 6. Experiment showing that the malonate residue remains intact in the cleavage of the cyclopropane ring during the retro-Bingel reaction.

reversibility for the first and second reduction steps on the CV time scale of 100 mV s^{-1}. This behavior is different from the CV response of the previously studied bis{[(ethoxy)carbonyl]methyl} 1,2-methano[70]fullerene-71,71-dicarboxylate,[17c, 18] which displayed an electrochemically irreversible second reduction. The fact that the latter mono-adduct with four ester groups in the side chains of the methano addend undergoes decomposition in the di-anionic state much more readily than its diester counterpart **10** further strengthens our hypothesis that the retro-Bingel reaction is enhanced by increasing the electron-withdrawing character of the substituents at the methano bridge.

CPE carried out on **10** at the second reduction potential (-1.44 V vs. Fc/Fc$^-$) was interrupted when charge corresponding to two electrons had been transferred. The solution was then re-oxidized at 0 V (25 % charge recovered). Analysis of the product mixture showed that the retro-Bingel reaction had occurred, producing C_{70} in 64 % yield with 21 % of the starting material remaining unreacted (Scheme 7). CPE at the

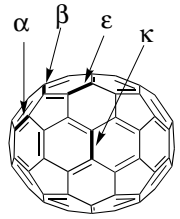


10 (64%)

Scheme 7. Retro-Bingel reaction of C_{70} mono-adduct **10**.

first reduction potential and between the first and second reduction potentials transferring 1 and 1.5 electron-equivalents, respectively, resulted in the production of only $\approx$1 % C_{70}. Interestingly, the chromatograms (HPLC) of the products of these reactions also revealed the presence of traces of the three constitutional bis-adducts of C_{70}, **11**, (±)-**12**, and (±)-**13**. Such evidence of an intermolecular reaction process was not observed in similar experiments with bis[bis(dialkoxycarbonyl)methano] adducts of C_{60}.[18, 21]

The bis-adducts, **11**, (±)-**12**, and (±)-**13** were subjected to similar electrochemical conditions as was **10**. Recall that under these conditions, the analogous bis-adducts of C_{60} isomerize by the "walk-on-the-sphere" rearrangement (Scheme 2).[21] It was thus interesting to learn whether a two-electron CPE of C_{70} bis-adducts would also lead to isomerization, or would it induce addend removal *via* the retro-Bingel reaction. The former would possibly provide a route for the preparation of otherwise unattainable Bingel-type bis-adducts with addends across β, ε, or even κ bonds (Scheme 8).[4, 37]



Scheme 8. The four different types of 6,6-bonds in C_{70}.[4, 37]

The results of the electrochemical transformations of **10**, **11**, (±)-**12**, and (±)-**13** by two-electron CPE, followed by re-oxidation, are presented in Table 2. It is evident that **11** undergoes only minimal conversion, producing 3 % mono-adduct and practically no isomerization to other bis-adducts. Compound (±)-**13**, on the other hand, forms the mono-adduct as the major product in 39 % yield and, similar to **11**, shows nearly no tendency to isomerize. The third constitutional isomer (±)-**12**, again behaves differently. The main reaction pathway of the dianion of (±)-**12** is the retro-Bingel reaction, but a small portion also isomerizes to the dianions of **11** and (±)-**13**. Whether the dianion of (±)-**12** looses directly an addend or isomerizes preferentially to the dianion of (±)-**13** which then undergoes the retro-Bingel reaction could not be decided by our experiments so far.

Table 2. Distribution of products obtained by coulometric CPE of C_{70} mono- and bis-adducts in CH_2Cl_2 (+0.1 M Bu_4NPF_6) and re-oxidation.

2-electron CPE Starting material	Products [%]				
	C_{70}	**10**	**11**	(±)-**12**	(±)-**13**
10	64	21	< 1	< 1	< 1
11	< 1	3	92	< 1	< 1
(±)-**12**	2	27	4	31	6
(±)-**13**	5	39	–	1	28
1.5-electron CPE Starting material	**Products [%]**				
	C_{70}	**10**	**11**	(±)-**12**	(±)-**13**
10	1	81	< 1	< 1	< 1
11	< 1	< 1	94	< 1	< 1
(±)-**12**	–	7	3	71	4
(±)-**13**	1	5	4	20	32

When these results are compared to those obtained with the corresponding C_{60} bis-adducts,[18, 21] it becomes obvious that the electrochemistry of the C_{70} bis-adducts is quite different. Either the dianions of the bis-adducts of C_{70} are stable or the retro-Bingel reaction is much faster than isomerization. Isomerization plays only a minor role in the electrochemical reactions of the dianions of the C_{70} bis-adducts, whereas it is the major reaction of the dianions of the Bingel-type bis-adducts of C_{60}.

The observation that the dianion of bis-adduct **11** is more stable than the di-anions of its isomers (±)-**12** and (±)-**13** is in full agreement with the results of our previous CV-studies.[17c] There, it was shown that only the Bingel-type C_{70} bis-adduct with an addition pattern corresponding to **11** (but slightly different malonate addends) has a reversible second reduction wave, whereas the bis-adducts with addition patterns corresponding to (±)-**12** and (±)-**13**, respectively, showed an irreversible second electron transfer on the CV time scale.

Since the retro-Bingel reaction predominates over the "walk-on-the-sphere" rearrangement under the conditions of two-electron CPE, it was presumed that in order to effect isomerization, a lower number of electrons should be transferred. Thus, the C_{70} bis-adducts were subjected to coulometrically controlled 1.5-electron-per-molecule electrolysis (Table 2). Whereas the behavior of **11** did not reflect the change in conditions, (±)-**12** underwent retro-Bingel reaction to a small extent, while still producing only very small amounts of the two other constitutional isomers. Isomer (±)-**13**, on the other hand, displayed the most striking example of rearrangement occurring on the C_{70} spheroid with the

0947-6539/00/0612-2188 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 12

generation of (±)-**12** in 20% yield. Further variations of the number of electrons transferred per molecule of (±)-**13** confirmed that at room temperature (298 K) the ideal condition for isomerization of (±)-**13** is 1.5-electron CPE.

The 1.5-electron CPE results may be explained using the known stability of the dianions from the previous experiments. It is assumed that the small quantities of mono-adduct **10** formed during 1.5-electron CPE of (±)-**12** and (±)-**13** result from the decomposition of the corresponding dianions. The dianion of (±)-**12** is also responsible for the formation of the rearranged bis-adducts **11** and (±)-**13** in 3% and 4% yield, respectively. On the other hand, the mono-anion of (±)-**12** seems to be stable on the time scale of CPE. The same can be said for the mono-anion of bis-adduct **11**. Compound (±)-**13** shows again a different behavior. As already pointed out, it isomerizes to (±)-**12** under 1.5-electron CPE in 20% yield. Since the dianion of (±)-**13** undergoes preferentially the retro-Bingel reaction, it must be the mono-anion that isomerizes slowly to the mono-anion of (±)-**12**. Once this mono-anion is formed, it is stable and does not further isomerize. This behavior of the mono-anion of (±)-**13** explains the fact that only traces of **11** are formed under these conditions, which was further confirmed by conducting a 1-electron CPE on isomer (±)-**13**. In this case, part of the starting material isomerized to (±)-**12** (4%), and another small part rearranged to **11** (1%), whereas nearly no retro-Bingel reaction to the mono-adduct **10** took place (1%). Most of the starting material (29%) was recovered unchanged.

It must be remarked that the HPLC analysis of the electrolysis products of **11**, (±)-**12**, and (±)-**13** showed additional peaks that do not correspond to C_{70} or its known Bingel-type mono- and bis-adducts. These peaks correspond to as yet uncharacterized species. Intensive efforts are now underway to isolate and characterize these compounds, which we are hoping could be the first examples of Bingel bis-adducts with addends at β-, ε-, or κ-type 6,6-bonds. The different reactivity of the anions of Bingel-type bis-adducts of C_{60} and C_{70} in coulometric CPE adds another example to the increasing number of experiments in which substantial differences in the chemical behavior between the two fullerenes have become apparent.[25, 38–40]

Conclusion

The results presented in this study clearly demonstrate that it is possible to electrochemically remove in high yields a bis(ethoxycarbonyl)methano addend from the C_{60} sphere in the presence of a variety of other addends, including cyclohexene, pyrrolidine, and benzocyclobutene rings fused to 6,6-bonds. This investigation establishes the bis(alkoxycarbonyl)-methano addend (Bingel addend) as a versatile new protecting and directing group in fullerene chemistry which is readily introduced and removed. This protecting/directing group strategy, coupled with tether-directed remote functionalization, should provide access to many new C_{60} multiple adducts featuring novel addition patterns and functions.[14b, 15]

The experiments reported in this paper revealed not only substantial differences in the electrochemical reactivity of three constitutionally isomeric Bingel-type bis-adducts of C_{70}. They also showed that the retro-Bingel reaction and the "walk-on-the-sphere" rearrangement during coulometric CPE do not necessarily occur along the same pathway for Bingel bis-adducts of C_{60} and C_{70}. Thus, this study provides another interesting example of the differences in chemical behavior between the two most abundant fullerenes.

Experimental Section

General methods: Reagents and solvents were purchased reagent-grade and used without further purification. C_{60} (purity: >99%) was purchased from Southern Chemical Group, LLC, Tucker, GA 30085-0527, USA. Compounds **1**[6a], (±)-**7**[30b], **14**[26], **15**[27], **16**[28], **17**[29], and 4,4′-dimethoxybenzophenone *N*-tosylhydrazone[41] were synthesized according to literature procedures. All reactions were performed in standard glassware under N_2. Evaporation and concentration in vacuo were done at water aspirator pressure, and compounds were dried at 10^{-2} Torr. Column chromatography: SiO_2 60 (230–400 mesh, 0.040–0.063 mm) from E. Merck and SiO_2-*H* from Fluka. TLC glass plates coated with SiO_2 60 F254 from E. Merck; visualization by UV light. Preparative and analytical HPLC of C_{60} and C_{70} bis-adducts: Knauer HPLC Pump 64 with preparative pump head and vacuum on-line degasser, electrical injection valve AA A0619, and variable wavelength monitor from Knauer; all chromatograms recorded at ambient temperature with a fixed detector wavelength at $\lambda =$ 310 nm; preparative HPLC-column: Macherey-Nagel Nucleosil 100-7 silica gel (7 μm, 250 × 21 mm I.D.); analytical HPLC-column: Macherey-Nagel Nucleosil 100-7 silica gel (5 μm, 250 mm × 4 mm I.D.). Analytical HPLC of electrolysis samples: Waters instrument equipped with a 515 pump and a 476 tunable UV absorbance detector using a Lichrosorb Si 60 (5 μm, 250 × 4 mm I.D.) column with toluene as eluent. Melting points: Büchi Melting Point B-540, uncorrected. UV/Vis spectra: Varian Cary-5 spectrophotometer. IR spectra: Perkin Elmer 1600-FTIR. NMR spectra: Bruker AM 500 at 298 K, with solvent peaks as reference. FAB-MS: VG ZAB 2SEQ instrument, 3-nitrobenzyl alcohol as matrix. Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH-Zürich.

(±)-Diethyl 65,66-dimethoxy-1,2-([1,2]benzeno)-33,50-methano[60]fullerene-61,61-dicarboxylate ((±)-4) and diethyl 65,66-dimethoxy-1,2-([1,2]benzeno)-18,36-methano[60]fullerene-61,61-dicarboxylate (9): To a solution of **14** (150 mg, 0.175 mmol), diethyl malonate (0.08 mL, 0.5 mmol), and I_2 (189 mg, 0.75 mmol) in PhMe/CH_2Cl_2 (600 mL/100 mL), DBU (0.2 mL, 2.0 mmol) was slowly added and the mixture was stirred for 12 h. Plug filtration (SiO_2; CH_2Cl_2) and column chromatography (SiO_2; CH_2Cl_2) afforded (±)-**4** (25 mg, 14%) and **9** (20 mg, 10%). Preparative HPLC yielded analytically pure (±)-**4** (eluent PhMe, injection volume 500 μL ($c =$ 2.1 mg mL^{-1}), flow rate 8.0 mL min^{-1}, retention time 38 min) and **9** (eluent PhMe, injection volume 500 μL ($c =$ 2 mg mL^{-1}), flow rate 8.0 mL min^{-1}, retention time 56 min).

(±)-4: Analytical HPLC purity control (eluent PhMe, flow rate 2.0 mL min^{-1}, retention time 6.5 min); m.p. >250 °C; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 702 (sh, 300), 622 (sh, 700), 479 (2500), 251 nm (120 000 mol^{-1} dm^3 cm^{-1}); IR (KBr): $\tilde{\nu} =$ 2978, 2922, 1745, 1478, 1281, 1044, 522 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta =$ 7.59 (s, 1H), 7.40 (s, 1H), 4.61–4.57 (m, 2H), 4.45 (q, $J =$ 7.1 Hz, 2H), 4.13 (s, 3H), 4.05 (s, 3H), 1.51 (t, $J =$ 7.1 Hz, 3H), 1.14 (t, $J =$ 7.1 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta =$ 163.57, 163.53, 157.16, 156.23, 156.14, 155.95, 151.81, 151.77, 148.26, 147.99, 147.90, 147.78, 147.74, 147.32, 147.27, 147.25, 147.22, 147.17, 147.12, 146.91, 146.75, 146.33, 146.18, 146.06, 145.95, 145.58, 145.32, 145.30, 145.22, 125.17, 145.02, 144.88, 144.58, 144.34, 144.31, 144.09, 144.08, 144.03, 144.02, 143.73, 143.53, 143.38, 143.34, 143.31, 143.24, 143.04, 142.82, 142.39, 142.37, 142.03, 141.84, 141.72, 141.59, 141.28, 141.11, 141.02, 140.62, 139.65, 139.52, 138.87, 138.76, 138.71, 106.80, 106.75, 71.43, 71.12, 63.55, 63.35, 63.28, 63.22, 63.16, 56.58, 56.51, 51.12, 14.28, 14.14; MS (FAB): *m/z* (%): 1015 ([M^+], 57), 720 (C_{60}^+, 100).

9: Analytical HPLC purity control (eluent PhMe, flow rate 2.0 mL min^{-1}, retention time 9.8 min); m.p. >250 °C; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 462 (5000), 255 nm (50 000 mol^{-1} dm^3 cm^{-1}); IR (KBr): $\tilde{\nu} =$ 2967, 2922, 1744,

1477, 1455, 1238, 1094, 1044, 522 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta =$ 7.36 (s, 2H), 4.41 (q, $J = 7.1$ Hz, 4H), 4.04 (s, 6H), 1.37 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 163.21$, 154.30, 154.07, 151.68, 148.48, 147.90, 147.81, 147.23, 146.93, 146.85, 146.56, 146.51, 146.33, 145.18, 145.17, 144.80, 144.76, 144.56, 144.45, 143.89, 143.80, 143.55, 143.16, 142.90, 142.84, 142.58, 142.46, 141.62, 141.02, 140.27, 139.05, 137.66, 106.55, 77.88, 71.68, 70.30, 63.11, 56.50, 50.81, 14.14; MS (FAB): *m/z* (%): 1014 ([M^+], 57), 720 (C_{60}^+, 100).

(±)-Diethyl 63,64-bis[(acetoxy)methyl]-1,2-(but[2]eno)-33,50-methano[60]fullerene-61,61-dicarboxylate ((±)-5): To a solution of **15** (420 mg, 0.46 mmol) and diethyl 2-bromomalonate (0.11 mL, 0.69 mmol) in PhMe (350 mL), DBU (0.13 mL, 0.92 mmol) was added and the solution was stirred for 2 h. Plug filtration (SiO_2; $CH_2Cl_2 \rightarrow CH_2Cl_2$/MeOH 95:5) and column chromatography (SiO_2; CH_2Cl_2/MeOH 98:2) gave (±)-**5** (35 mg, 7%) as the second fraction. Preparative HPLC yielded analytically pure (±)-**5** (eluent PhMe/AcOEt 49:1, injection volume 500 µL ($c =$ 2.1 mg mL^{-1}), flow rate 8.0 mL min^{-1}, retention time 17 min). Analytical HPLC purity control (eluent CH_2Cl_2, flow rate 2.0 mL min^{-1}, retention time 7.9 min); m.p. >250 °C; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 701 (sh, 290), 630 (sh, 650), 475 (3150), 244 nm (125000 mol^{-1} dm^3 cm^{-1}); IR (KBr): $\tilde{\nu} = 2977$, 2922, 1741, 1367, 1229, 1016, 522 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta =$ 5.24 (br s, 2H), 5.15 (br s, 2H), 4.61 – 4.57 (m, 2H), 4.45 – 4.38 (m, 2H), 4.16 (d, $J = 14.2$ Hz, 1H), 4.10 (d, $J = 14.2$ Hz, 1H), 3.94 (d, $J = 13.9$ Hz, 1H), 3.88 (d, $J = 13.9$ Hz, 1H), 2.10 (s, 3H), 1.94 (s, 3H), 1.51 (t, $J = 7.1$ Hz, 3H), 1.38 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 170.93$, 170.79, 163.52, 163.47, 148.72, 148.30, 148.28, 148.15, 148.02, 147.59 (2×), 147.56, 147.53 (2×), 147.47, 147.39, 146.79, 146.74, 146.21, 146.05, 145.95, 145.77, 145.49, 145.20, 144.85, 144.47, 144.36, 144.34, 144.20 (2×), 144.14, 144.11, 143.94, 143.81, 143.65, 143.25, 143.10, 143.05, 142.44, 142.00, 141.83, 141.70, 141.54, 141.49, 141.25, 140.76, 139.50, 138.78, 137.62, 136.38 (2×), 71.10, 70.93, 65.76, 65.24, 63.33, 63.15, 62.38, 62.30, 50.90, 43.21, 42.05, 20.09, 20.72, 14.82, 14.11; MS (FAB): *m/z* (%): 1077 ([M^+], 48), 720 (C_{60}^+, 97); $C_{77}H_{24}O_8$ (1077.0): calcd: C 85.87, H 2.25; found: C 85.90, H 2.42.

(±)-Diethyl 63-methyl-1,2-(methaniminomethano)-33,50-methano[60]fullerene-61,61-dicarboxylate ((±)-6): To a solution of **16** (260 mg, 0.33 mmol), diethyl malonate (0.06 mL, 0.4 mmol), and I_2 (126 mg, 0.5 mmol) in PhMe/CH_2Cl_2 (250 mL/200 mL), DBU (0.15 mL, 1.0 mmol) was slowly added. After 2 h, diethyl malonate (0.12 mL, 0.8 mmol), I_2 (252 mg, 1.0 mmol), and DBU (0.3 mL, 2.0 mmol) were added again and the solution was stirred for another 2 h. Plug filtration (SiO_2; $CH_2Cl_2 \rightarrow$ CH_2Cl_2/MeOH 9:1) and column chromatography (SiO_2; CH_2Cl_2) provided (±)-**6** (40 mg, 13%). Preparative HPLC yielded analytically pure (±)-**4** (eluent PhMe, injection volume 500 µL (c = 1.9 mg mL^{-1}), flow rate 8.0 mL min, retention time 75 min). Analytical HPLC purity control (eluent PhMe/AcOEt 9:1, flow rate 1.0 mL min^{-1}, retention time 4.7 min); m.p. >250 °C; UV/Vis (CH_2Cl_2): λ_{max} (ε) 700 (sh, 290), 620 (sh, 700), 473 (2500), 247 nm (105000 mol^{-1} dm^3 cm^{-1}); IR (KBr): $\tilde{\nu} = 2968$, 2922, 2773, 1743, 1229, 526 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta =$ 4.62-4.58 (m, 2H), 4.42 (dq, $J = 7.1$ Hz, 1.5 Hz, 2H), 4.41 (d, $J = 9.2$ Hz, 1H), 4.35 (d, $J = 9.2$ Hz, 1H), 4.23 (d, $J = 9.3$ Hz, 1H), 4.17 (d, $J = 9.3$ Hz, 1H), 2.94 (s, 3H), 1.51 (t, $J = 7.1$ Hz, 3H), 1.38 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 163.53$ (2×), 156.87, 155.82, 155.63, 148.44, 148.09, 148.06, 148.01, 147.98, 147.88, 147.48, 147.46, 147.40 (2×), 147.30, 147.19, 146.47, 146.31, 146.29, 146.15, 146.03, 145.88, 145.46, 145.29, 145.14, 144.99, 144.64, 144.55, 144.39, 144.28, 144.20, 144.16, 144.15, 143.91, 143.82, 143.71, 143.37 (2×), 143.16, 143.10, 143.06, 143.02, 142.50, 142.00, 141.77, 141.69, 141.48, 141.46, 140.80, 139.90, 139.73, 139.47, 139.06, 138.80, 137.91, 136.75, 135.94, 71.10, 70.59, 70.15, 69.46, 63.31, 63.15, 56.57, 51.04, 41.61, 14.27, 14.12; MS (FAB): *m/z* (%): 936 ([M^+], 35), 720 (C_{60}^+, 50).

(±)-Diethyl 64,65-dimethoxy-1,2-methano-33,50-(methano[1,2]benzenomethano)[60]fullerene-69,69-dicarboxylate ((±)-8): To a solution of **1** (470 mg, 0.54 mmol) in PhMe (300 mL), 1,2-bis(bromomethyl)-4,5-dimethoxybenzene (230 mg, 0.71 mmol) and Bu_4NI (580 mg, 1.57 mmol) were added and the mixture was heated to reflux for 16 h. After cooling to 20 °C, the mixture was washed with water (3×) and the organic phase dried ($MgSO_4$). Column chromatography (SiO_2; PhMe/CH_2Cl_2 2:1) afforded five fractions of which the second contained (±)-**8** (12 mg, 2%). Preparative HPLC yielded analytically pure (±)-**8** (eluent PhMe, injection volume 500 µL ($c = 2.0$ mg mL^{-1}), flow rate 8.0 mL min^{-1}, retention time 37 min). Analytical HPLC purity control (eluent PhMe, flow rate 2.0 mL min^{-1}, retention time 9.8 min); m.p. >250 °C; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 700 (sh, 250), 620 (sh, 700), 475 (3000), 242 nm (142000 mol^{-1} dm^3 cm^{-1}); IR (KBr): $\tilde{\nu} = 2922$, 1745, 1505, 1450, 1280, 1111, 1022, 522 cm^{-1}; ^1H NMR (500 MHz, $Cl_2DCCDCl_2$, 80 °C): $\delta = 7.19$ (br s, 1H), 7.05 (br s, 1H), 4.58 – 4.45 (m, 2H), 4.58 (br q, $J = 7.1$ Hz, 2H), 4.35 – 4.25 (m, 2H) 4.34 (q, $J = 7.1$ Hz, 2H), 3.97 (s, 3H), 3.90 (s, 3H), 1.57 (br t, $J = 7.1$ Hz, 3H), 1.31 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 163.56$ (2×), 159.00, 157.69, 157.68, 148.71, 148.64 (2×), 148.27, 148.14, 147.57 (2×), 147.48, 146.80, 146.72, 146.00, 145.76, 145.73, 145.47, 145.21, 144.86, 144.48, 144.34 (2×), 144.13 (2×), 143.92, 143.82, 143.63, 143.22, 143.01, 142.53, 142.42, 142.38, 141.82, 141.69, 141.52, 141.44, 140.78, 138.83, 130.07, 129.02, 128.21, 111.53, 71.03, 70.88, 66.07, 65.62, 63.30, 63.13, 56.28, 56.24, 50.81, 45.20, 14.27, 14.11; MS (FAB): *m/z* (%): 1043 ([M^+], 65), 720 (C_{60}^+, 55).

Tetraethyl 1,2:41,58-bis(methano)[70]fullerene-71,71,72,72-tetracarboxylate (11), (±)-tetraethyl 1,2:56,57-bis(methano)[70]fullerene-71,71,72,72-tetracarboxylate ((±)-12), and (±)-tetraethyl 1,2:67,68-bis(methano)[70]-fullerene-71,71,72,72-tetracarboxylate ((±)-13): The bis-adduct mixture **11**, (±)-**12**, and (±)-**13** was prepared according to the literature.[6b] After isolation of the mono-adduct fraction from the crude reaction mixture by column chromatography (SiO_2; PhMe), the regioisomeric bis-adducts were separated by column chromatography (SiO_2-*H*; PhMe/hexane 8:2) to yield, in the order of elution: **11** (11%), (±)-**12** (47%), and (±)-**13** (13%). The purity of each fraction was checked by HPLC (SiO_2, PhMe, flow rate 1.0 mL min^{-1}).

61,61-Bis(*p*-methoxyphenyl)-1,2-methano[60]fullerene (17): Compound **17** was synthesized by a slightly modified literature procedure.[30b] C_{60} (1.2 g, 1.58 mmol) was dissolved in PhMe (600 mL), then BuLi (1.75 mL 1.6 M solution in hexane, 2.8 mmol) was added. A solution of 4,4′-dimethoxybenzophenone *N*-tosylhydrazone in PhMe (100 mL) was added, and the mixture was heated to reflux for 1 h. After cooling to 20 °C, plug filtration (SiO_2; PhMe) yielded the crude product which was further purified by column chromatography (SiO_2; PhMe/hexane 3:2 → 2:1). The mono-adduct fraction that contained a mixture of the 6,6-closed and 6,5-open mono-adducts was dissolved in PhMe (200 mL) and heated to reflux for 10 h. Finally, the solution was evaporated to dryness, dissolved in CH_2Cl_2, and re-precipitated with hexane to yield pure **17** (550 mg, 37%). Analytical data are in agreement with the literature.[30b]

1,1′-(Ethane-1,2-diyl) 3,3′-diethyl bis(malonate): Ethane-1,2-diol (250 mg, 4.03 mmol), ethyl 3-chloro-3-oxopropanoate (1.8 g, 12.1 mmol), and C_5H_5N (0.96 g, 12.1 mmol) were mixed in CH_2Cl_2/THF (60 mL/10 mL), and the solution was stirred for 12 h at 20 °C. The mixture was washed with saturated aqueous NH_4Cl solution (2×), dried ($MgSO_4$), and evaporated to dryness. Column chromatography (SiO_2; CH_2Cl_2/AcOEt 3:1) yielded the desired product (1.013 g, 87%) as a colorless oil. IR (film): $\tilde{\nu} = 2985$, 1754, 1733, 1446, 1410, 1328, 1271, 1189, 1151, 1035, 979, 867, 841, 787, 681 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 4.31$ (s, 4H), 4.14 (q, $J = 7.5$ Hz, 4H), 3.34 (s, 4H), 1.22 (t, $J = 7.5$ Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 165.90$, 165.77, 62.28, 61.11, 40.82, 13.55; MS (EI): *m/z* (%): 291 [*M*H$^+$]; $C_{12}H_{18}O_8$ (290.3): calcd: C 49.65, H 6.25; found: C 49.42, H 6.03.

(±)-*endo*,*endo*-61,62-(Ethane-1,2-diyl) 61,62-diethyl 1,2:16,17-bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate ((±)-21): To a solution of C_{60} (300 mg, 0.416 mmol), 1,1′-(ethane-1,2-diyl) 3,3′-diethyl bis(malonate) (145 mg, 0.5 mmol), and I_2 (264 mg, 1.04 mmol) in PhMe (600 mL), DBU (0.4 mL, 2.5 mmol) was slowly added under N_2 at 20 °C and the mixture was stirred for 12 h. Plug filtration (SiO_2; CH_2Cl_2) and column chromatography (SiO_2; CH_2Cl_2) yielded (±)-**21** (60 mg, 16%) as red-brown solid. M.p. >250 °C; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 699 (260), 634 (sh, 480), 459 (2140), 314 (34700), 253 nm (99300 mol^{-1} dm^3 cm^{-1}); IR (film): $\tilde{\nu} = 2967$, 1745, 1439, 1362, 1230, 1097, 1050, 751, 525 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 5.27$ (br d, $J = 11.2$ Hz, 2H), 4.52 (q, $J = 7.1$ Hz, 4H), 4.26 (br d, $J =$ 11.2 Hz, 2H), 1.47 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta =$ 163.91, 163.24, 146.71, 146.58, 145.58, 145.56, 145.55, 145.50, 145.43, 145.13, 144.96, 144.90, 144.56, 144.41, 144.14, 143.91, 143.65, 143.36, 142.49, 142.46, 142.45, 141.96, 141.07, 141.06, 140.87, 140.83, 140.55, 135.31, 128.75, 71.80, 68.56, 63.93, 63.57, 49.80, 14.22; (FAB): *m/z* (%): 1006 ([M^+], 75), 720 (C_{60}^+, 100).

Electrochemistry: Fullerene mono- and bis-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 ref. [31]). The cell was degassed and pumped to 10^{-6} mm Hg. The solvent, CH_2Cl_2 (14 mL), which had also been degassed and pumped to the same pressure, was then vapor-transferred into the cell, directly from P_2O_5. Prior to CPE, cyclic

0947-6539/00/0612-2190 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 12

voltammetry was performed using a glassy carbon- or a Pt-disk working electrode to obtain the reduction potentials versus a Ag wire pseudo-reference electrode. The latter was separated from the bulk solution using a vycor tip. Unless otherwise specified, exhaustive CPE was conducted at 293 K on a Pt mesh (100 mesh, 6.5 cm^2) working electrode at 100 mV more negative than the second reduction peak potential. The solution was then exhaustively re-oxidized at 0 V. 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 either toluene or carbon disulfide. TLC, HPLC, ^{1}H NMR, and/or UV/VIS spectroscopy were used to identify the products.

1,1′-(Ethane-1,2-diyl) 3,3′-diethyl 2,2-([60]fullerene-1,2-diyl)bis(malonate) (22): Bis-adduct (±)-**21** (19.5 mg, 0.019 mmol) was electrolyzed at the first reduction potential and 1.8 C were transferred to the solution. In a second reduction step at the second reduction potential, another 2.8 C were transferred to the solution. After exhaustive re-oxidation at 0 V, 1.9 C were recovered. Column chromatography (SiO_2-*H*, CH_2Cl_2) yielded C_{60} (25%), (±)-**21** (18%), and **22** (17%). **22**: M.p. >250 °C; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 686 (280), 484 (2100), 426 (2700), 325 (41000), 259 nm (141000 $mol^{-1}\,dm^3\,cm^{-1}$); IR (KBr): $\tilde{\nu}$ = 2967, 1746, 1233, 526 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.73–4.71 (m, 2H), 4.57 (q, J = 7.1 Hz, 2H), 4.56–4.54 (m, 2H), 4.21 (q, J = 7.1 Hz, 2H), 1.49 (t, J = 7.1 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 166.36, 166.10, 163.47, 163.29, 145.29, 145.21, 145.20, 145.13, 145.10, 145.02, 144.92, 144.83, 144.70, 144.69, 144.65, 144.58, 143.90, 143.87, 143.10 (2×), 143.04, 143.03, 142.96, 142.21, 142.19, 141.88, 141.86, 140.97 (2×), 139.37, 138.81, 71.38, 64.39, 63.58, 62.69, 61.73, 51.84, 41.28, 14.22, 14.11; MS (FAB): *m/z* (%): 1008 ([M^+], 38), 720 (C_{60}^+, 97); $C_{72}H_{16}O_8$ (1008.9): calcd: C 85.72, H 1.60; found: C 85.49, H 1.47.

Acknowledgements

We thank Mr. S. Siefken for the preparation of the C_{70}-adducts and the Swiss National Science Foundation as well as the US National Science Foundation (grant CHE-9816503) for financial support. A donation of pure C_{70} by Hoechst AG (Germany) is gratefully acknowledged.

[1] a) A. Hirsch, *The Chemistry of the Fullerenes*, Thieme, Stuttgart, **1994**; b) A. Hirsch, *Top. Curr. Chem.* **1999**, *199*, 1–65.
[2] S. Samal, S. K. Sahoo, *Bull. Mat. Sci*. **1997**, *20*, 141–230.
[3] F. Diederich, C. Thilgen, *Science* **1996**, *271*, 317–323.
[4] a) C. Thilgen, A. Herrmann, F. Diederich, *Angew. Chem.* **1997**, *109*, 2362–2374; *Angew. Chem. Int. Ed.* **1997**, *36*, 2268–2280; b) C. Thilgen, F. Diederich, *Top. Curr. Chem*. **1999**, *199*, 135–171.
[5] a) F. Diederich, R. Kessinger, *Acc. Chem. Res.* **1999**, *32*, 537–545; b) F. Diederich, R. Kessinger in *Templated Organic Synthesis* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, **1999**, 189–218.
[6] a) C. Bingel, *Chem. Ber.* **1993**, *126*, 1957–1959; b) C. Bingel, H. Schiffer, *Liebigs Ann.* **1995**, 1551–1553.
[7] M. Prato, M. Maggini, *Acc. Chem. Res.* **1998**, *31*, 519–526.
[8] C. Bingel, presentation at the conference 'New Perspectives in Fullerene Chemistry and Physics', Rome (Italy) **1994**.
[9] J.-F. Nierengarten, V. Gramlich, F. Cardullo, F. Diederich, *Angew. Chem.* **1996**, *108*, 2242–2244; *Angew. Chem. Int. Ed.* **1996**, *35*, 2101–2103.
[10] X. Champs, A. Hirsch, *J. Chem. Soc. Perkin Trans. 1* **1997**, 1595–1596
[11] See references cited in ref. [5]; see also: J.-P. Bourgeois, P. Seiler, M. Fibbioli, E. Pretsch, F. Diederich, L. Echegoyen, *Helv. Chim. Acta* **1999**, *82*, 1572–1595.
[12] F. Diederich, M. Gómez-López, *Chem. Soc. Rev.* **1999**, *28*, 263–277; see also: J. F. Nierengarten, C. Schall, J.-F. Nicoud, B. Heinrich, D. Guillon, *Tetrahedron Lett.* **1998**, *39*, 5747–5750.
[13] a) R. Schwenninger, T. Müller, B. Kräutler, *J. Am. Chem. Soc.* **1997**, *119*, 9317–9318; b) I. Lamparth, C. Maichle-Mössmer, A. Hirsch, *Angew. Chem.* **1995**, *107*, 1755–1757; *Angew. Chem. Int. Ed.* **1995**, *34*, 1607–1609.
[14] a) Y.-Z. An, G. A. Ellis, A. L. Viado, Y. Rubin, *J. Org. Chem.* **1995**, *60*, 6353–6361; b) W. Qian, Y. Rubin, *Angew. Chem*. **1999**, *111*, 2504–2508; *Angew. Chem. Int. Ed*. **1999**, *38*, 2356–2360.
[15] a) F. Cardullo, L. Isaacs, F. Diederich, J.-P. Gisselbrecht, C. Boudon, M. Gross, *Chem. Commun.* **1996**, 797–799; b) F. Cardullo, P. Seiler, L. Isaacs, J.-F. Nierengarten, R. F. Haldimann, F. Diederich, T. Mordasini-Denti, W. Thiel, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Helv. Chim. Acta* **1997**, *80*, 343–371.
[16] T. Da Ros, M. Prato, F. Novello, M. Maggini, M. De Amici, C. De Micheli, *Chem. Commun.* **1997**, 59–60.
[17] For previous studies, see: a) C. Boudon, J.-P. Gisselbrecht, M. Gross, L. Isaacs, H.-L. Anderson, R. Faust, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 1334–1344; b) J.-F. Nierengarten, T. Habicher, R. Kessinger, F. Cardullo, F. Diederich, V. Gramlich, J.-P. Gisselbrecht, C. Boudon, M. Gross, *Helv. Chim. Acta* **1997**, *80*, 2238–2276; c) C. Boudon, J.-P. Gisselbrecht, M. Gross, A. Herrmann, M. Rüttimann, J. Crassous, F. Cardullo, L. Echegoyen, F. Diederich, *J. Am. Chem. Soc.* **1998**, *120*, 7860–7868.
[18] For a preliminary communication of parts of this work, see:R. Kessinger, J. Crassous, A. Herrmann, M. Rüttimann, L. Echegoyen, F. Diederich, *Angew. Chem.* **1999**, *110*, 2022–2025; *Angew. Chem. Int. Ed.* **1999**, *37*, 1919–1922.
[19] For earlier hints at the reversibility of the Bingel reaction, see: a) A. Hirsch, I. Lamparth, T. Grösser, H. R. Karfunkel, *J. Am. Chem. Soc.* **1994**, *116*, 9385–9386; b) F. Arias, Y. Yang, L. Echegoyen, Q. Lu, S. R. Wilson, in *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials* (Eds.: K. M. Kadish, R. S. Ruoff), The Electrochemical Society, Pennington, **1995**, pp. 200–212; c) M. Keshavarz-K., B. Knight, R. C. Haddon, F. Wudl, *Tetrahedron* **1996**, *52*, 5149–5159.
[20] J. Crassous, J. Rivera, N. S. Fender, L. Shu, L. Echegoyen, C. Thilgen, A. Herrmann, F. Diederich, *Angew. Chem.* **1999**, *111*, 1716–1721; *Angew. Chem. Int. Ed.* **1999**, *38*, 1613–1617.
[21] R. Kessinger, M. Gómez-López, C. Boudon, J.-P. Gisselbrecht, M. Gross, L. Echegoyen, F. Diederich, *J. Am. Chem. Soc.* **1998**, *120*, 8545–8546.
[22] L. Isaacs, F. Diederich, R. F. Haldimann, *Helv. Chim. Acta* **1997**, *80*, 317–342.
[23] L. Echegoyen, J.-P. Bourgeois, F. Cardullo, F. Diederich, M. Gómez-López, A. Herrmann, R. Kessinger, M. Rüttimann in *Supramolecular Science: Where it is and Where it is Going* (Eds.: R. Ungaro, E. Dalcanale), NATO ASI Series, *Vol.* 527, Kluwer, Dordrecht, **1998**, pp. 39–53.
[24] F. Diederich, U. Jonas, V. Gramlich, A. Herrmann, H. Ringsdorf, C. Thilgen, *Helv. Chim. Acta* **1993**, *76*, 2445–2453.
[25] A. Herrmann, M. W. Rüttimann, T. Gibtner, C. Thilgen, F. Diederich, T. Mordasini, W. Thiel, *Helv. Chim. Acta* **1999**, *82*, 261–289.
[26] T. Ishida, K. Shinozuka, T. Nogami, S. Sasaki, M. Iyoda, *Chem. Lett*. **1995**, 317–318.
[27] Y.-Z. An, A. L. Viado, M.-J. Acre, Y. Rubin, *J. Org. Chem.* **1995**, *60*, 8330–8331.
[28] M. Maggini, G. Scorrano, M. Prato, *J. Am. Chem. Soc.* **1993**, *115*, 9798–9799.
[29] S. Shi, K. C. Khemani, Q. C. Li, F. Wudl, *J. Am. Chem. Soc.* **1992**, *114*, 10656–10657.
[30] a) A. Hirsch, I. Lamparth, H. R. Karfunkel, *Angew. Chem*. **1994**, *106*, 453–455; *Angew. Chem. Int. Ed.* **1994**, *33*, 437–438; b) F. Djojo, A. Herzog, I. Lamparth, F. Hampel, A. Hirsch, *Chem. Eur. J.* **1996**, *2*, 1537–1547.
[31] P. L. Boulas, Y. Zuo, L. Echegoyen, *Chem. Commun.* **1996**, 1547–1548.
[32] L. Isaacs, F. Diederich, *Helv. Chim. Acta* **1993**, *76*, 2454–2463.
[33] P. Timmerman, H. L. Anderson, R. Faust, J.-F. Nierengarten, T. Habicher, P. Seiler, F. Diederich, *Tetrahedron* **1996**, *52*, 4925–4947.
[34] For recent examples of fullerene derivatives with fused pyrrolidine rings, see: a) H. Imahori, H. Yamada, S. Ozawa, K. Ushida, Y. Sakata, *Chem. Commun.* **1999**, 1165–1166; b) P. A. Lidell, D. Kuciauskas, J. P. Sumida, B. Nash, D. Nguyen, A. L. Moore, T. A. Moore, D. Gust, *J. Am. Chem. Soc.* **1997**, *119*, 1400–1405; c) K. B. Simonsen, V. V. Konovalov, T. A. Konovalova, T. Kawai, M. P. Cava, L. D. Kispert, R. M. Metzger, J. Becher, *J. Chem. Soc. Perkin Trans. 2* **1999**, 657–665; d) T. Da Ros, M. Prato, M. Carano, P. Ceroni, F. Paolucci, S. Roffia, *J. Am. Chem. Soc.* **1998**, *120*, 11645–11648; e) T. Da Ros, M. Prato, D. Guldi, E. Alessio, M. Ruzzi, L. Pasimeni, *Chem. Commun*. **1999**, 635–636; f) M. Maggini, D. M. Guldi, S. Mondini, G. Scorrano,

F. Paolucci, P. Ceroni, S. Roffia, *Chem. Eur. J.* **1998**, *4*, 1992 – 2000; g) L. Gan, J. Jiang, W. Zhang, Y. Su, Y. Shi, C. Huang, J. Pan, M. Lü, Y. Wu, *J. Org. Chem.* **1998**, *63*, 4240 – 4247; h) A. Kurz, C. M. Halliwell, J. J. Davis, H. A. O. Hill, G. W. Canters, *Chem. Commun*. **1998**, 433 – 434; i) N. Martín, I. Pérez, L. Sánchez, C. Seoane, *J. Org. Chem*. **1997**, *62*, 5690 – 5695; j) G. Schick, M. Levitus, L. Kvetko, B. A. Johnson, I. Lamparth, R. Lunkwitz, B. Ma, S. I. Khan, M. A. Garcia-Garibay, Y. Rubin, *J. Am. Chem. Soc*. **1999**, *121*, 3246 – 3247.

[35] a) Y. Rubin, S. Khan, D. I. Freedberg, C. Yeretzian, *J. Am. Chem. Soc.* **1993**, *115*, 344 – 345; b) P. Belik, A. Gügel, J. Spickermann, K. Müllen, *Angew. Chem.* **1993**, *105*, 95 – 97; *Angew. Chem. Int. Ed.* **1993**, *32*, 78 – 80; c) B. Kräutler, M. Puchberger, *Helv. Chim. Acta* **1993**, *76*, 1626 – 1631.

[36] For recent examples of fullerene derivatives with fused cyclohexene rings, see: a) ref. [14b]; b) M. Ohno, Y. Shirakawa, S. Eguchi, *Synthesis* **1998**, 1812 – 1816; c) M. Ohno, T. Azuma, S. Kojima, Y. Shirakawa, S. Eguchi, *Tetrahedron* **1996**, *52*, 4983 – 4994; d) R. F. Haldimann, F.-G. Klärner, F. Diederich, *Chem. Commun*. **1997**, 237 – 238.

[37] A. Herrmann, F. Diederich, C. Thilgen, H.-U. ter Meer, W. H. Müller, *Helv. Chim. Acta* **1994**, *77*, 1689 – 1706.

[38] P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc. Chem. Commun.* **1995**, 683 – 684.

[39] M. S. Meier, G. W. Wang, R. C. Haddon, C. P. Brock, M. A. Lloyd, J. P. Selegue, *J. Am. Chem. Soc*. **1998**, *120*, 2337 – 2342.

[40] A. F. Kiely, R. C. Haddon, M. S. Meier, J. P. Selegue, C. P. Brock, B. O. Patrick, G.-W. Wang, Y. Chen, *J. Am. Chem. Soc.* **1999**, *121*, 7971 – 7972.

[41] W. R. Bamford, R. R. Stevens, *J. Chem. Soc.* **1952**, 4735 – 4740.

Received: December 7, 1999 [F2177]

  0947-6539/00/0612-2192 $ 17.50+.50/0