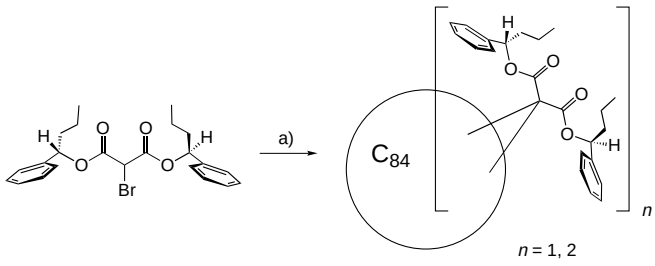
[9] The structure of **8** has been determined by X-ray crystallography: B. Weberndörfer, Dissertation, Universität Würzburg, in preparation.
[10] It was mentioned by a referee that the CPh_2 groups could be considered as dianionic ligands. The metal centers would then be Rh^{II} and Rh^{IV}. The total electron count would be unaltered due to this formalism.
[11] T. V. Ashworth, M. J. Chetcuti, L. J. Farrugia, J. A. K. Howard, J. C. Jeffery, R. Mills, G. N. Pain, F. G. A. Stone, P. Woodward, *ACS Symp. Ser.* **1981**, *155*, 299 – 313.
[12] Reviews: a) P. M. Maitlis, *J. Organomet. Chem.* **1995**, *500*, 239 – 249; b) P. M. Maitlis, H. C. Long, R. Quyoum, M. L . Turner, Z.-Q. Wang, *Chem. Commun.* **1996**, 1 – 8.
[13] J. Vicente, M. T. Chicote, *Inorg. Synth.* **1998**, *32*, 172 – 177.
[14] The ^1H and ^{13}C NMR data of the phenyl groups were omitted for simplicity.

Chemistry of C_{84}: Separation of Three Constitutional Isomers and Optical Resolution of D_2-C_{84} by Using the "Bingel – Retro-Bingel" Strategy**

Jeanne Crassous, José Rivera, Nicolette S. Fender, Lianhe Shu, Luis Echegoyen*, Carlo Thilgen, Andreas Herrmann, and François Diederich*

Although C_{84} is the third most abundant fullerene,[1] its chemistry remains remarkably unexplored. Computational studies revealed that this higher fullerene has 24 theoretically possible constitutional isomers that obey the isolated pentagon rule (IPR), with a D_2- and a D_{2d}-symmetrical isomer being the most stable ones.[2] These two isomers are indeed the most abundant ones in the C_{84} fraction of fullerene soot, with a ratio of D_2-C_{84}:D_{2d}-C_{84} of approximately 2:1, but their chromatographic separation is extremely difficult and, for several years, they had only been isolated and characterized as a mixture by ^{13}C NMR spectroscopy[3] and other methods. The successful separation by recycling high performance liquid chromatography (HPLC) and full characterization of these two isomers was only reported recently by Shinohara and coworkers.[4] The structure of the D_{2d} isomer was unambiguously proven by Balch et al. who prepared the $[(\eta^2\text{-}D_{2d}\text{-}C_{84})Ir(CO)Cl(PPh_3)_2]\cdot 4C_6H_6$ complex and solved its X-ray crystal structure.[5] This is the only characterized derivative of a C_{84} isomer reported thus far. Although four possible structures exist that fit the ^{13}C NMR data of the major D_2 isomer,[3, 4] the experience with the isomers of another higher fullerene, C_{78},[6] and preliminary 2D NMR (INADEQUATE) data of the C_{84} isomers[7a] suggest that the compound with the calculated lowest energy structure is the one isolated in all published work. Both ^{13}C NMR studies[3c, 7] and the analysis of endohedral ^3He complexes of the C_{84} fraction of the fullerene soot by ^3He NMR spectroscopy[8] have provided evidence for the presence of minor amounts of additional isomers, but none of them have been isolated to date. Here, we describe a powerful new protocol to isolate pure constitutional isomers of higher fullerenes by the intermediacy of defined covalent adducts,[9] by using the recently introduced Bingel – retro-Bingel reaction sequence.[10, 11] This protocol takes advantage of the fact that covalent adducts of isomeric higher fullerenes are much easier to separate than the parent unfunctionalized carbon spheroids. By this method we not only isolated the two known major constitutional isomers of C_{84} but also succeeded in the first isolation and spectroscopic characterization of a third minor isomer in pure form. Furthermore, we describe the application of this protocol to the optical resolution of D_2-C_{84}.[12] Also, contradictory reports in the literature concerning the electrochemistry of C_{84} isomers[13, 14] are clarified.

The C_{84} fraction (52 mg, 0.052 mmol)[15] of soot enriched in higher fullerenes, provided by Hoechst AG, was treated in *o*-dichlorobenzene (*o*-DCB) at 20 °C with bis[(*S*)-1-phenylbutyl]-2-bromomalonate[16] in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; Scheme 1). Subsequent purification by column chromatography (SiO_2, CH_2Cl_2/hexane (1/1) → CH_2Cl_2) yielded four fractions containing, according to matrix-assisted laser-desorption-ionization time-of-flight mass spectrometry (MALDI-TOF MS), pure C_{84}, monoadducts, bis-adducts, and tris-adducts, respectively. The monoadduct fraction was further separated by HPLC ((*S*,*S*)-Whelk-O, 250 × 10 mm, hexane/CH_2Cl_2 (7/3), flow rate 2 mL min^{-1}) to give four main products **Ia** – **Id** of which two (**Ia** (0.8 mg, 1 % and **Id** (2.5 mg, 3.5 %)) were isolated and characterized



Scheme 1. Formation of mono- and bis-adducts of various C_{84} isomers by Bingel cyclopropanation. a) C_{84}, DBU, *o*-DCB, Ar, 20 °C, 14 h.

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(Table 1). The bis-adduct fraction was separated (HPLC, Macherey-Nagel Nucleosil 100-7 SiO_2, 250 × 21 mm, hexane/CH_2Cl_2 (7/3), flow rate 6 mL min^{-1}) to give six main products **IIa**–**IIf**, of which four (**IIa** (13.8 mg, 15%), **IId** (6 mg, 7%), **IIe** (3 mg, 3.5%), and **IIf** (7 mg, 8%) were isolated and characterized. The symmetries of these compounds were determined by ^{1}H and ^{13}C NMR spectroscopy (Table 2).

Table 1. Products isolated from the Bingel reaction of the C_{84} fraction in the fullerene soot (Scheme 1).

Adducts	HPLC fraction	Yield [%]	Symmetry[a]	Derivative of	Assigned structure
mono-add.[b]	**Ia**	1	C_2	D_{2d}-C_{84}	**1**
	Id	3.5	C_1	new isomer	none
bis-add.[c]	**IIa**	15	D_2	D_{2d}-C_{84}	**2**
	IId	7	C_2	D_2-C_{84}	**3a**–**8a**
	IIe	3.5	C_2	D_2-C_{84}	**3b**–**8b**
	IIf	8	C_1	new isomer	none

[a] The symmetry assignment was based on the number of signals seen for the PhCHO groups (^{1}H and ^{13}C NMR) and for the bridgehead and methano bridge C(sp^3) atoms (^{13}C NMR). [b] Fractions **Ib** and **Ic** are the main products but were extremely difficult to separate. [c] Fractions **IIb** and **IIc** are severely overlapping and could not be separated; the amount of material in the mixture of these fractions is comparable to that in fraction **IIa**.

Based on the experiences with the functionalization of other higher fullerenes, nucleophilic cyclopropanation of C_{84} was expected to occur preferentially at the 6-6 bonds (bonds between two 6-membered rings) that are the most curved ones and have the highest π bond order.[9] In both D_2-C_{84} and D_{2d}-C_{84} there are ten 6-6 bonds of more pronounced local curvature[9b, 15, 17] and three of these bonds also possess the highest π bond order (Figure 1).[17] All possible structures of mono- and bis-adducts generated by the addition of either an achiral or a chiral malonate to the ten most curved bonds in both isomers were constructed with molecular models and their symmetries determined. This analysis revealed that the C_2-symmetrical mono-adduct from fraction **Ia** could correspond to one of four structures: three derivatives of D_{2d}-C_{84} and one of D_2-C_{84}. An additional, extremely valuable structural selection criterion was provided by the circular dichroism (CD) spectra of the nonracemic compounds. Optically active fullerene derivatives with achiral fullerene cores or functionalization patterns display weak Cotton effects ($\Delta\varepsilon$ values around 1–10 M^{-1} cm^{-1}), while those having inherently chiral cores or functionalization patterns show large Cotton effects with $\Delta\varepsilon$ values of up to 200 M^{-1} cm^{-1} and higher.[9, 16] The CD spectrum of the mono-adduct from fraction **Ia** exhibited only weak Cotton effects with $\Delta\varepsilon$ values up to 3 M^{-1} cm^{-1}. Of the three possible C_2-symmetrical mono-adducts of achiral D_{2d}-C_{84}, only structure **1**, which results from nucleophilic addition to the C(32)–C(53) bond with the highest π bond order, displays an achiral functionalization pattern. Therefore, this structure is assigned to the mono-adduct in fraction **Ia** (Scheme 2). It is noteworthy that formation of the $[(\eta^2$-D_{2d}-$C_{84})Ir(CO)Cl(PPh_3)_2]\cdot 4C_6H_6$ complex had also occurred at this bond.[5]

Table 2. Selected physical data of C_{84} mono- and bis-adducts.[a]

1 (product from fraction **Ia**): UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, [M^{-1} cm^{-1}]) = 704 (380), 637 (670), 555 (sh, 1200), 525 (sh, 1500), 478 (2300), 435 (sh, 3500), 410 (sh, 6700), 384 (11500), 340 (sh, 10000), 296 (21800), 276 (24900), 255 (sh, 38100); ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.46–7.29 (m, 10H), 6.15 (t, J = 7.1 Hz, 2H), 2.16–2.08 (m, 2H), 2.00–1.82 (m, 2H), 1.49–1.21 (m, 4H), 0.98 (t, J = 7.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125.8 MHz, 40 mM [Cr(acac)$_3$], acac = acetylacetonate): δ = 163.70, 148.00, 147.79, 146.39, 145.98, 145.81, 144.70, 143.65, 143.57, 143.39, 143.27, 143.23, 142.61, 142.58, 142.37, 141.80, 141.40, 141.27, 139.16, 138.85, 138.48, 138.46, 136.13, 135.86, 135.38, 135.00, 134.83, 134.02, 133.76, 133.73, 128.36, 128.26, 126.84, 79.57, 58.95, 37.69, 31.71, 18.65, 13.91.

2 (product from fraction **IIa**): UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, [M^{-1} cm^{-1}]) = 720 (2300), 646 (1800), 570 (2600), 485 (sh, 5300), 458 (10400), 430 (13700), 395 (31500), 363 (sh, 17400), 310 (sh, 17400), 310 (sh, 53300), 286 (87900), 268 (sh, 105500), 257 (sh, 111000); ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.47–7.28 (m, 20H), 6.22 (t, J = 7 Hz, 4H), 2.22–2.14 (m, 4H), 2.01–1.94 (m, 4H), 1.48–1.37 (m, 4H), 1.33–1.22 (m, 4H), 1.01 (t, J = 7.4 Hz, 12H); ^{13}C NMR ($CDCl_3$, 125.8 MHz, 40 mM [Cr(acac)$_3$]): δ = 163.94, 146.72, 146.51, 143.65, 143.58, 143.26, 143.21, 142.03, 142.01, 141.68, 141.56, 139.86, 139.85, 138.92, 137.86, 136.39, 136.24, 136.03, 135.74, 134.60, 134.56, 128.39, 128.28, 128.01, 126.90, 126.31, 126.28, 79.65, 58.29, 49.31, 37.76, 18.71, 13.70.

Product from fraction **IId**:[b] UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, [M^{-1} cm^{-1}]): = 620 (2100), 550 (4400), 470 (8300), 447 (10700), 418 (14500), 399 (15600), 377 (17300), 327 (sh, 31600), 305 (sh, 43600), 264 (93300); ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.32–7.14 (m, 20H), 6.06–6.02 (m, 4H), 2.09–2.00 (m, 4H), 1.89–1.81 (m, 4H), 1.47–1.42 (m, 4H), 1.37–1.26 (m, 4H), 0.95 (t, J = 7.4 Hz, 6H), 0.94 (t, J = 7.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125.8 MHz, 40 mM [Cr(acac)$_3$]): δ = 163.66, 163.53, 148.53, 146.54, 146.07, 145.48, 144.83, 144.68, 144.37, 144.20, 144.09, 143.97 (2×), 143.76, 142.93, 142.38, 142.17, 141.91, 141.40, 141.28, 141.10 (2×), 140.24, 140.15, 139.77, 139.53, 139.18, 138.98, 138.84, 138.81, 138.75, 137.98, 137.94, 136.87, 136.21, 136.14, 134.58, 134.33, 133.99, 133.17, 133.15, 132.13, 131.87, 131.59, 128.30, 128.22, 128.10, 126.94, 126.69, 126.64, 79.51, 79.21, 58.78, 56.23, 47.12, 37.65, 37.58, 18.56, 13.56.

Product from fraction **Id**: UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, [M^{-1} cm^{-1}]) = 569 (2200), 482 (sh, 5400), 454 (6900), 405 (10500), 358 (13000), 320 (sh, 18800), 267 (sh, 46800); ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.40–7.27 (m, 10H), 6.09–6.05 (m, 2H), 2.11–2.05 (m, 2H), 1.91–1.85 (m, 2H), 1.50–1.30 (m, 4H), 0.98 (t, J = 7.5 Hz, 6H), 0.96 (t, J = 7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125.8 MHz, 40 mM [Cr(acac)$_3$]): δ = 163.81, 161.41, 152.91, 148.00, 147.55, 147.19, 147.07, 146.91, 146.36, 146.23, 146.21, 145.96, 144.44, 143.57, 143.44, 143.34, 142.94, 142.84, 142.70, 142.56, 142.18, 141.89, 141.88, 141.83, 141.46, 141.41, 141.36, 141.30, 140.11, 140.06, 140.03, 139.48, 139.16, 139.14, 139.08, 138.90, 138.88, 138.75, 138.49, 135.82, 135.48, 135.07, 133.72, 133.44, 132.99, 132.96, 132.70, 131.46, 128.38, 128.36, 128.26, 128.14, 126.88, 126.72, 79.39, 79.34, 59.31, 58.37, 37.71, 37.61, 18.66, 18.30, 13.91, 13.64.

Product from fraction **IIf**: UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε, [M^{-1} cm^{-1}]): = 704 (600), 617 (sh, 1300), 502 (sh, 4700), 457 (7800), 399 (20200), 390 (sh, 20000), 364 (sh, 20000), 320 (sh, 35400), 295 (55400), 265 (sh, 75900); ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.40–7.19 (m, 20H), 6.13 (t, J = 7.0 Hz, 1H), 6.09 (t, J = 7.0 Hz, 1H), 5.95 (t, J = 7.0 Hz, 1H), 5.91 (t, J = 7.0 Hz, 1H), 2.17–2.00 (m, 2H), 2.00–1.82 (m, 4H), 1.82–1.70 (m, 2H), 1.50–1.20 (m, 8H), 0.97 (t, J = 7.4 Hz, 3H), 0.95 (t, J = 7.4 Hz, 6H), 0.91 ("t", J = 7.4 Hz, 3H), 0.88 ("t", J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz, 40 mM [Cr(acac)$_3$]): δ = 163.95, 163.90, 163.40, 163.29, 147.29, 147.24, 147.20, 147.05, 146.77, 146.67, 146.48, 146.31, 146.13, 145.85, 145.75, 145.49, 145.37, 145.35, 145.23, 144.94, 144.90, 144.86, 144.73, 144.63, 144.49, 144.45, 144.41, 144.09, 143.43, 143.21, 143.19, 141.90, 141.75, 141.71, 141.60, 141.52, 141.49, 139.50, 139.42, 139.22, 139.19, 138.79, 138.74, 138.36, 138.33, 138.14, 138.11, 137.87, 137.59, 137.01, 136.89, 136.62, 136.36, 135.25, 135.19, 134.97, 134.94, 134.79, 134.69, 134.48, 134.43, 133.49, 133.44, 132.96, 132.83, 131.56, 131.43, 128.70, 128.65, 128.23, 128.14, 128.09, 128.07, 127.88, 126.84, 126.76, 126.56, 126.39, 79.26, 79.22, 79.19, 79.02, 58.94, 56.60, 56.52, 49.11, 37.74, 37.54, 37.50, 18.55, 18.52, 18.47, 18.42, 13.81, 13.55, 13.49, 13.47.

[a] CD spectra and correct MALDI-TOF mass spectra were also obtained for each compound. [b] The data for the products from fraction **IId** and **IIe** are very similar; the latter will be reported in a full paper.

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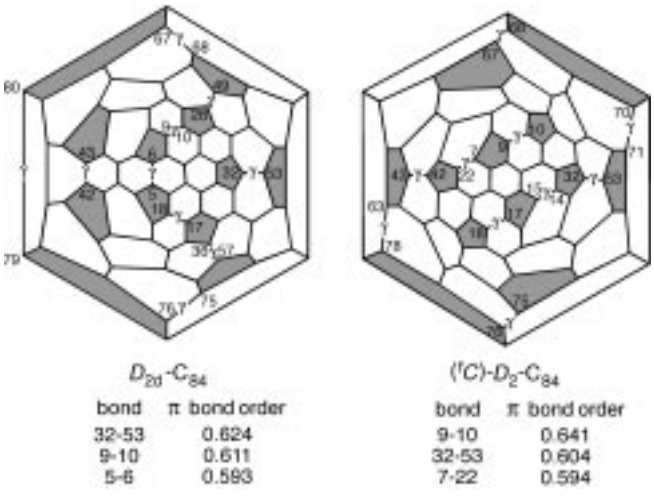


Figure 1. Schlegel diagrams of D_{2d}-C_{84} and (^{f}*C*)-D_2-C_{84} showing the ten most curved bonds, which are of the γ type according to a previously introduced qualitative model to evaluate local curvature.[15] The highest π bond orders in D_{2d}-C_{84} are at the γ-type bonds C(32)–C(53) (π bond order = 0.624), C(9)–C(10) (0.611), and C(5)–C(6) (0.593), and in D_2-C_{84} at the γ-type bonds C(9)–C(10) (0.614), C(32)–C(53) (0.604), and C(7)–C(22) (0.594).[17] The IUPAC numbering scheme for the C_{84} isomers[18] as well as the previously introduced configurational descriptor system (^{f}*C*; f = fullerene, *C* = clockwise) to describe the absolute configuration of inherently chiral fullerenes or fullerenes with a chiral functionalization pattern are used.[19]

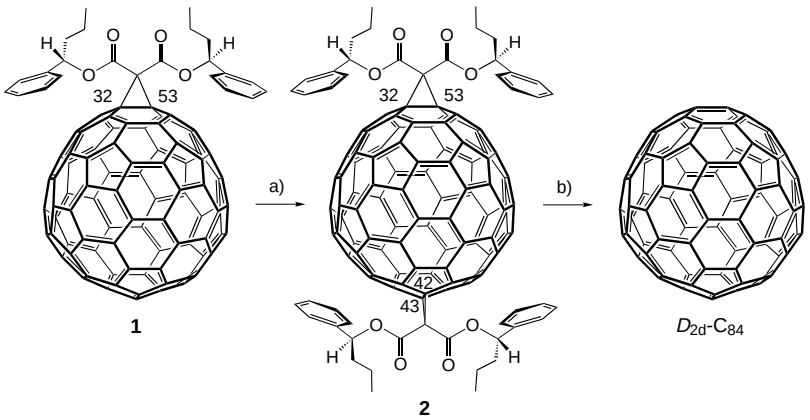
The D_2-symmetrical bis-adduct from fraction **IIa** also displayed only weak Cotton effects ($\Delta\varepsilon$ values lower than $3\,\text{M}^{-1}\text{cm}^{-1}$) in the CD spectrum and, in view of its abundance (Table 1) and the results of the retro-Bingel reaction described below, must be a derivative of D_{2d}-C_{84} with an achiral functionalization pattern. The CD and NMR spectral properties unambiguously support the formation of bis-adduct **2**, which results from cyclopropanation at C(32)–C(53) and C(42)–C(43) (Scheme 2). It is reasonable to assume that **2**, which features the remarkable structure of a D_2-symmetrical bis-adduct having an achiral fullerene core, is formed by cyclopropanation of **1**. Compounds **1** and **2** are the first fully characterized organic derivatives of C_{84}.

The products of fractions **IId** and **IIe** are C_2-symmetrical bis-adducts, which feature mirror-image CD spectra with large Cotton effects. Such spectra are characteristic of a pair of diastereoisomers, with the chiroptical contributions of the enantiomeric, inherently chiral fullerene cores or functionalization patterns largely dominating those of the chiral addends.[16] The UV/Vis spectra of the two diastereoisomers (Table 2) differ considerably from those of the D_{2d}-C_{84} bis-adduct **2**, which suggests that they are derivatives of D_2-C_{84}. This was clearly confirmed after the retro-Bingel reaction and the electrochemical investigations on the parent fullerene enantiomers (see below). A total of six C_2-symmetrical constitutional isomers, each consisting of a pair of diastereoisomers (**3a**/**3b**–**8a**/**8b**) are possible structures for the products from fractions **IId** and **IIe**, which cannot be further distinguished at this stage on the basis of the number of NMR resonances.[20]

The UV/Vis spectra of the C_1-symmetrical mono- and bis-adducts of fractions **Id** and **IIf** again differed significantly from those of the derivatives of both D_2- and D_{2d}-C_{84}. This first indication that these products originated from cyclopropanation of a hitherto unknown constitutional isomer of C_{84} was further substantiated by the retro-Bingel reaction and electrochemical investigations described below.

Electrochemical investigations by cyclic voltammetry (CV) or Osteryoung square wave voltammetry (OSWV) in CH_2Cl_2 (+0.12 M Bu_4NPF_6) revealed that the mono- (fractions **Ia** and **Id**) and bis-adducts (fractions **IIa** and **IId**–**f**) of C_{84} each underwent at least four reductions, with only the first one being fully reversible at 298 K in most cases. Chemical reversibility improves considerably at lower temperature.

The retro-Bingel reaction was performed in CH_2Cl_2 in a degassed H-cell on the compounds from fractions **Id**, **IIa**, and **IId**–**f**. The mono- and bis-adducts were reduced by controlled potential electrolysis (CPE) on a Pt mesh (100 mesh, 6.5 cm^2) working electrode at potentials 0.1 V more negative than the third reduction potential, and then re-oxidized at 0 V versus Ag. For the mono-adduct, the net charge transferred after reduction followed by re-oxidation corresponded to two electrons per molecule, while for the bis-adducts, six electrons were transferred per molecule. Almost all of the formed C_{84} precipitated when the re-oxidized solution was left overnight. The C_{84} isomers were purified by chromatography on neutral alumina (toluene) to afford the isolated products in yields between 22 and 94%. Analysis of this material by MALDI-TOF MS, however, revealed that the retro-Bingel reaction had not only provided the pure C_{84} isomers, but that the corresponding methanofullerenes $C_{84}CH_2$, which resulted from addition of the CH_2Cl_2 solvent to the fullerene di- or trianions, had also been formed in 10–20% relative yield during CPE. The electrosynthesis of methanofullerenes from C_{60} and dihalogenated reagents such as CH_2I_2 had been reported previously by some of us.[21] The methanofullerenes could be separated from the new isomer and from the D_{2d}- and D_2-C_{84} isomers by HPLC, either on a Buckyclutcher column (250 × 4.6 mm; toluene, flow rate 2 mL min^{-1}) or on a Lichrosorb Si60



Scheme 2. Formation of the D_{2d}-C_{84} bis-adduct **2** from mono-adduct **1** and generation of the parent fullerene by retro-Bingel reaction. a) Bis[(*S*)-1-phenylbutyl]-2-bromomalonate, DBU, *o*-DCB. b) Controlled potential electrolysis, CH_2Cl_2.

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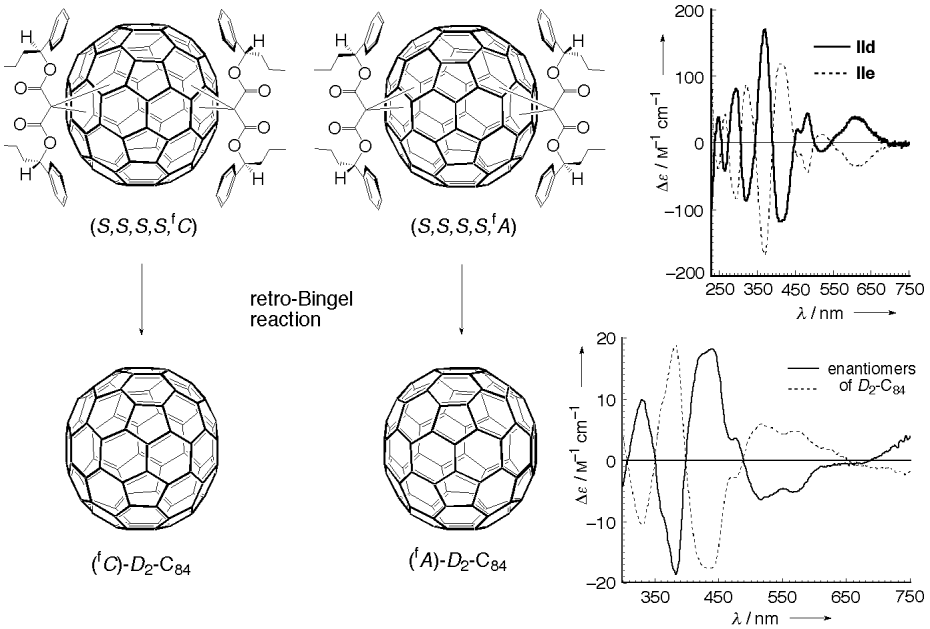
SiO_2 column (250 × 10 mm; hexane/toluene (9/1), flow rate 1 mL min^{-1}).

The retro-Bingel reaction of the product in fraction **IIa** produced the known D_{2d} isomer (Scheme 2), which displayed its characteristic bright green color with the corresponding UV/Vis spectrum[4] and was CD-inactive. Controlled potential electrolysis of the diastereoisomeric pair from fractions **IId** and **IIe** gave rise to the two enantiomers of D_2-C_{84}, and their mirror image CD spectra (Scheme 3) correspond nicely to those reported by Hawkins et al. for samples obtained by kinetic resolution through asymmetric osmylation.[12] With $\Delta\varepsilon$ values up to 20 M^{-1}cm^{-1}, the inherently chiral D_2-C_{84} enantiomers feature much weaker Cotton effects than the enantiomers of the smaller, inherently chiral D_2-symmetrical C_{76} for which $\Delta\varepsilon$ values up to 200 M^{-1}cm^{-1} have been measured.[11] This may be a consequence of the fact that the chirality arises in D_2-C_{76} from its oblong, helically twisted structure,[6] while D_2-C_{84} is rather round-shaped and only slightly distorted from achiral D_{2d}-C_{84}. A theoretical CD spectrum has been calculated by Zerbetto and co-workers for D_2-C_{84}[22] but, unlike the case of C_{76},[23] it does not allow an accurate determination of the absolute configuration by comparison with the experimental spectrum.



Scheme 3. Preparation of the pure enantiomers of D_2-C_{84} by retro-Bingel reaction of the bis-adducts from fractions **IId** and **IIe**, and CD spectra of the diastereoisomeric bis-adducts (top right) as well as of the fullerene enantiomers (bottom right) in CH_2Cl_2. The absolute configurations of the fullerene spheroids (^fC and ^fA; f = fullerene, C = clockwise, A = anticlockwise) reflect the structural drawings, but have not been assigned experimentally.

The retro-Bingel reaction of the products from fractions **Id** and **IIf** yielded a novel C_{84} isomer that is CD-inactive and whose UV/Vis spectra differ from those of the D_2- and D_{2d}-C_{84} isomers (Figure 2). Unfortunately, the sample amounts were not sufficient for a structural characterization by ^{13}C NMR spectroscopy, so the symmetry of the isomer remains unknown.

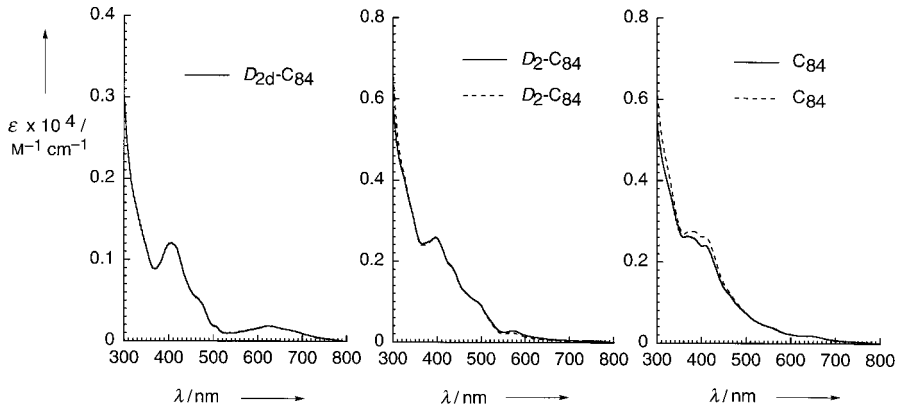


Figure 2. UV/Vis spectra of D_{2d}-C_{84} (left), the two enantiomers of D_2-C_{84} (middle), and the new achiral isomer of as yet unidentified structure (right). For the new isomer, the UV/Vis spectra of both samples prepared by retro-Bingel reaction of the products from fractions **Id** and **IIf**, are shown.

The redox properties of the three constitutional C_{84} isomers were investigated in dry pyridine (+0.1 M Bu_4NPF_6) by OSWV in a micro-electrochemical cell.[24] Table 3 shows the peak potentials (in V versus ferrocene/ferrocenium (Fc/Fc^+)). The potentials for the first four reductions of the D_{2d} and D_2 isomers are quite similar as is the relative constant spacing (about 400 mV) between the different reduction waves. A nicely resolved, much more negatively shifted fifth reduction wave separated by some 800 mV from the fourth wave, is additionally observed for the D_{2d} isomer, which clearly indicates that the lowest unoccupied molecular orbital (LUMO) is very close to being doubly degenerate with a LUMO+1 much higher in energy. The redox properties of the third, new isomer differ significantly from those of the D_2 and D_{2d} isomers, with a large gap being observed between the second and third reduction waves.

Table 3. Peak potentials E_p for constitutional isomers of C_{84} measured by OSWV in pyridine (+ 0.1 M Bu_4NPF_6).

E_p	Assigned C_{84} isomers				
	this work[a]			ref. [14]	
	D_2	D_{2d}	new isomer	D_2	D_{2d}
E^{1}[b]	−0.56	−0.55	−0.42	−0.65	−0.46
E^{2}	−0.88	−0.86	−0.73	−0.98	−0.77
E^{3}	−1.24	−1.20	−1.46	−1.34	−1.58
E^{4}	−1.67	−1.59	−1.90	−1.75	−1.98
E^{5}		−2.40			

[a] At 295 K. [b] Potential [V] versus Fc/Fc^+.

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This indicates that the LUMO is nondegenerate for this isomer.

The electrochemical data for the D_2 and D_{2d} isomers are in full agreement with those previously reported[13] except for a recent publication by Anderson et al.[14] The latter group investigated the electrochemistry of two isomers (Table 3) that were separated by HPLC and, on the basis of the relative abundances and previous work, were assigned the D_2- and D_{2d}-symmetrical structures. While the redox properties of the D_2 isomer match those reported here, the ones assigned to the D_{2d} isomer differ from those determined by us and others[13] for this fullerene and rather match those of what we call here the "new isomer". On the basis of our findings we conclude that Anderson et al. had not isolated D_{2d}-C_{84} but rather the "new isomer" in addition to the D_2-symmetrical one.

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A Polymer-Supported Phosphazine as a Stable and Practical Reagent in the Three-Component Synthesis of Substituted (Cyclopentadienyl)-tricarbonylrhenium Complexes**

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In recent years the use of reagents and catalysts bound to inorganic and organic solid supports has rapidly become an area of intense research activity,[1] since they present several obvious advantages over their soluble counterparts: they can be removed from the reaction mixture by simple filtration and, often, can be recycled and used again. Herein we report the preparation and the use of a polymer-bound stabilized diazocyclopentadiene ($C_5H_4N_2$) analogue, which can be used as a safe and storable source of $C_5H_4N_2$ in the synthesis of substituted cyclopentadienyl–$Re(CO)_3$ complexes.

The use of "free" $C_5H_4N_2$ in the synthesis of halogen-substituted cyclopentadienyl complexes of rhenium was

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