NMR (2.50×10^{-2} M): 8.85 (brs, 2H), 8.69 (brs, 2H), 7.90 (brs, 2H), 7.83 (brs, 2H), 7.69 (brd, $^3J = 7$ Hz, 2H), 7.32–7.50 (m, 4H), 7.11 (brt, $^3J = 7$ Hz, 2H), 6.83 (s, 2H), 6.64 (brd, $^3J = 7$ Hz, 2H), 5.93 (brs, 2H), 4.41(brs, 3H), 4.05 (brs, 4H), 3.89 (brs, 8H), 3.60–3.80 (m, 20H); ^{13}C NMR (2.50×10^{-2} M): $\delta = 154.9$, 150.8, 148.1, 147.2, 146.4, 142.3, 141.6, 134.6, 132.4, 131.5, 129.2, 127.0, 126.6, 126.5, 122.9, 114.9, 106.8, 71.5, 71.2, 70.5, 70.4, 70.2, 69.2, 64.9, 49.6. **9** · 2 PF_6: yield 60%; m.p. 270 °C (decomp); UV/Vis (1.60×10^{-2} M): λ_{max} (ε) = 472 nm (255); HR-MS: calcd for ($C_{98}H_{61}F_6N_3O_{12}P$) $[M - PF_6]^+$: 1136.3897, found: 1136.3885; ^1H NMR: (1.58×10^{-2} M): $\delta = 8.88$ (d, $^3J = 7$ Hz, 2H), 8.60 (d, $^3J = 7$ Hz, 2H), 8.27 (d, $^3J = 7$ Hz, 2H), 7.74 (brd, $^3J = 5$ Hz, 2H), 7.63 (d, $^3J = 8$ Hz, 2H), 7.54 (d, $^3J_{AB} = 8$ Hz, 2H), 7.50–7.40 (m, 5H), 7.36 (d, $^3J_{AB} = 8$ Hz, 2H), 7.20 (t, $^3J = 8$ Hz, 2H), 6.95 (s, 2H), 6.75 (d, $^3J = 8$ Hz, 2H), 5.78 (s, 2H), 5.10 (s, 2H), 4.15 (t, $^3J = 4$ Hz, 4H), 4.03 (t, $^3J = 4$ Hz, 4H), 3.90 (t, $^3J = 4$ Hz, 4H), 3.77 (t, $^3J = 4$ Hz, 4H), 3.59–3.72 (m, 16H); ^{13}C NMR (1.58×10^{-2} M): $\delta = 165.5$, 155.0, 151.0, 150.0, 146.5, 146.4, 134.7, 133.5, 132.7, 131.2, 131.1, 130.6, 130.4, 129.2, 127.8, 127.8, 127.2, 126.5, 123.0, 71.4, 70.4, 70.4, 70.1, 69.1, 65.8, 65.1.

[6] For tables listing the chemical shifts of selected resonances observed in the ^1H NMR spectra of **6** · 2 PF_6–**9** · 2 PF_6 at various concentrations, see the supporting information.

[7] Crystal data for **6** · 2 PF_6: $C_{44}H_{54}N_2O_{10} \cdot 2PF_6 \cdot 4PhH \cdot 0.5MeCN$, $M_r = 1393.8$, monoclinic, space group $C2/c$ (no. 15), $a = 22.497(5)$, $b = 17.912(4)$, $c = 34.814(10)$ Å, $\beta = 103.67(2)°$, $V = 13632(6)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.358$ g cm^{-3}, $\mu(Cu_{K\alpha}) = 13.8$ cm^{-1}, $F(000) = 5832$, $T = 213$ K. An orange block of dimensions $0.40 \times 0.40 \times 0.27$ mm was used for the data collected, and 3477 independent reflections were measured on a Siemens P4/RA diffractometer with $Cu_{K\alpha}$ radiation (graphite monochromator) and ω-scans. The structure was solved by direct methods. On account of a shortage of observed data, only the oxygen and nitrogen atoms of the ordered portions of the cyclophane were refined anisotropically—the carbon atoms, and all of the non-hydrogen atoms of the disordered section of one of the polyether arms (for which two partial occupancy orientations were identified), were refined isotropically. The aromatic rings were refined as idealized rigid bodies. The hexafluorophosphate counterions were disordered, and in each case two partial-occupancy orientations were identified with only the atoms of the major-occupancy orientations being refined anisotropically. The included benzene solvent molecules were distributed over a mixture of full- and partial-occupancy sites, and they were refined isotropically as idealized rigid bodies. The 50% occupancy MeCN molecule was refined isotropically. Refinement was by full matrix least-squares based on F^2 to give $R_1 = 0.114$ and $wR_2 = 0.305$ for 2202 independent observed reflections ($|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 106°$) and 496 parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101199. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] For a recent example of a cyclic homodimeric complex held together primarily by [N^+-H ··· O] and [C-H ··· O] hydrogen bonding, see P. R. Ashton, I. Baxter, S. J. Cantrill, M. C. T. Fyfe, P. T. Glink, J. F. Stoddart, A. J. P. White, D. J. Williams, *Angew. Chem.* **1998**, *110*, 1344–1347; *Angew. Chem. Int. Ed.* **1998**, *37*, 1294–1297.

[9] H. M. Colquhoun, C. A. O'Mahoney, D. J. Williams, *Polymer* **1993**, *34*, 218–221.

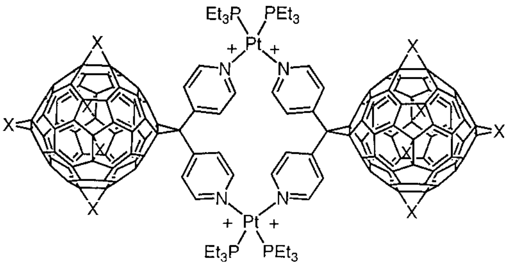
[10] The mean interplanar separation between the bipyridinium unit and the 1,5-dioxynaphthalene and resorcinol ring systems are 3.42 and 3.56 Å, respectively, and the N ··· N vector of the bipyridinium unit is inclined by 25° to the $OC_{10}H_6O$ axis of the 1,5-dioxynaphthalene ring system.

[11] We describe daisy chain arrays and assemblies as being acyclic [*a*] or cyclic [*c*] and use these two letters, along with numbers in the conventional manner, to define the nature and repeating unit, respectively, present in a particular supramolecular array or molecular assembly.[8] Note that only [*c*]daisy chains experience maximal (recognition) site occupancy (ref. [2b], p. 182–183) and that small [*c*]daisy chains (supermolecules) are also favored entropically with respect to large [*a*]daisy chains (supramolecular arrays).

Pt^{II}-Directed Self-Assembly of a Dinuclear Cyclophane Containing Two Fullerenes[**]

Tilo Habicher, Jean-François Nierengarten, Volker Gramlich, and François Diederich[*]

In order to develop fullerene-containing supramolecular assemblies and advanced materials,[1] C_{60} has been incorporated into multicomponent molecular systems such as rotaxanes,[2] catenanes,[3] and oligopyridine Ru^{II} complexes.[4] The properties of these C_{60} hybrids are encouraging and have generated our interest in the construction of even more complex two- and three-dimensional systems. To achieve this objective, we wished to take advantage of the self-assembly of multidentate ligand precursors with transition metal centers[5] which, in the hands of Fujita,[6] Stang,[7, 8] and others,[9] has led to the formation of some spectacular molecular architectures consisting of multinanometer-sized polynuclear molecular squares and three-dimensional molecular objects.[10] Here, we report the synthesis and X-ray crystal structure of the fullerene-containing rigid dinuclear cyclophane **1** which is obtained by self-assembly of the novel fullerene ligand **2** with Pt^{II} centers.



4 OTf$^-$ **1** X = $(EtO_2C)_2C$

In the preparation of **1**, dipyridylchloromethane **5** (obtained in two steps from 4-pyridinecarboxaldehyde **3** through **4**[11]) was treated under the conditions of the Bingel cyclopropanation method[12] to afford the fullerene monoadduct **6** (Scheme 1).[13] Attempts to complex ligand **6** with **7** led to a black, completely insoluble precipitate. In order to solubilize the expected complex, we prepared the yellow C_{2v}-symmetrical fullerene hexakis-adduct **2**[14] (m.p. > 270 °C) using the

$[cis\text{-}Pt(PEt_3)_2(OTf)_2]$ **7**

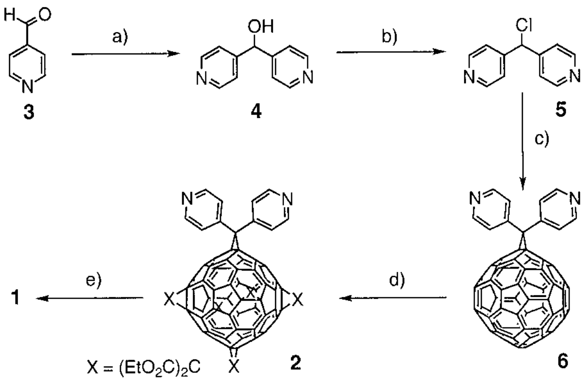
---

[*] Prof. F. Diederich, Dipl.-Chem. T. Habicher
Laboratorium für Organische Chemie, ETH-Zentrum
Universitätstrasse 16, CH-8092 Zürich (Switzerland)
Fax: (+41) 1-632-1109
E-mail: diederich@org.chem.ethz.ch

Dr. J.-F. Nierengarten
Institut de Physique et Chimie des Matériaux de Strasbourg C.N.R.S.
23 rue du Loess, F-67037 Strasbourg (France)

Dr. V. Gramlich
Laboratorium für Kristallographie, ETH-Zentrum
Sonneggstrasse 5, CH-8092 Zürich (Switzerland)

[**] This work was supported by the Swiss National Science Foundation and by a Kékulé doctoral stipend from the Stiftung Stipendienfonds des Verbandes der Deutschen Chemischen Industrie (T.H.). We thank Mr. P. Seiler for helpful discussions regarding the X-ray crystal structures and Dr. M. Sebova for NMR measurements.



Scheme 1. Preparation of cyclophane **1**. a) 4-Lithiopyridine, Et_2O, – 78 °C to 20 °C, 52 %; b) 1. methanesulfonyl chloride, NEt_3, CH_2Cl_2, 2. $CaCl_2$, Me_2SO, 62 %; c) C_{60}, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), toluene, 20 °C, 32 %; d) diethyl 2-bromomalonate, DBU, 9,10-dimethylanthracene, toluene, 35 %; e) **7**, CD_2Cl_2, 20 °C, N_2, 91 %.

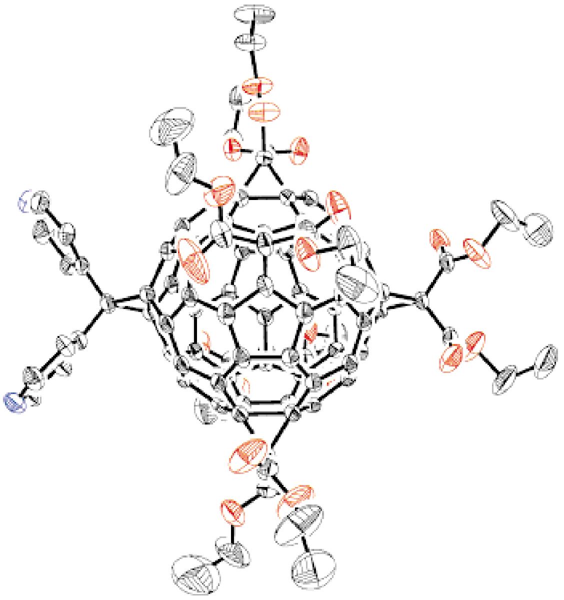


Figure 1. X-ray crystal structure of **2** (displacement ellipsoids are shown at the 30 % probability level). Only one of the two conformers is shown.

DMA-templated addition (DMA = 9,10-dimethylanthracene) of diethyl 2-bromomalonate.[15]

The pseudo-octahedral all-equatorial functional relationship of the addends in the hexakis-adduct **2** was proven by X-ray crystallography (Figure 1).[16] The unit cell of the crystal structure contains four fullerene molecules in two slightly different conformations, four benzene molecules, and ethyl acetate. The partially resolved ethyl acetate molecules and the flexible malonate esters give rise to some disorder in the structure. Despite this disorder, the dipyridylmethanofullerene core of the structure is well resolved. The C(pyr)-C-C(pyr) (pyr = pyridine) bond angle at the quaternary C atom of the dipyridylmethano bridge was 113(1)°.

By mixing an equimolar amount of **2** and **7** the tetracationic cyclophane **1** was obtained quantitatively as the tetrakis-triflate salt (triflate = trifluoromethane sulfonate). The multinuclear (^1H, ^{13}C, ^{19}F, ^{31}P) NMR spectroscopy data in CD_2Cl_2 were consistent with the formation of a single, highly symmetrical (D_{2h}) compound. The presence of triflate counterions is indicated by the typical ^{19}F NMR signal ($\delta = -79.1$), as well as the characteristic IR absorptions (1027, 1111, 1153 cm^{-1}). The ^{31}P NMR spectrum displayed one sharp singlet with appropriate Pt satellites for the equivalent P atoms. This resonance ($\delta = -4.56$) is upfield shifted relative to **7** ($\delta = 8.95$) because of the ligation by **2**. Particularly revealing are the ^1H NMR chemical shifts of the pyridyl and phosphane protons. The resonances of the α and β H atoms on the pyridyl rings in **1** are downfield shifted by $\Delta\delta = 0.62$ and 0.32, respectively, relative to their positions in **2**. The CH_2P signal is shifted upfield by $\Delta\delta = 0.16$, relative to its position in **7**. This upfield shift, which contrasts the downfield shifts of the CH_2P resonance reported for other molecular squares,[8a, b, d, f] can readily be explained by the shielding influence of the benzenoid rings in the neighboring fullerene hexakis-adducts in **1**.[17]

The X-ray crystal structure analysis unambiguously proved the [2+2] parallelogram-type structure[7a] of **1** (Figure 2).[16] Although the resolution of the structure is only moderate in view of 1) the high molecular weight of **1** ($C_{240}H_{176}F_{12}N_4O_{52}P_4Pt_2S_4$, $M_r = 4818$), 2) the small crystal size, 3) the disorder in the ethyl moieties of the phosphane and malonate units and in the triflate counterions, and 4) the inclusion of large amounts of unresolved solvent molecules (EtOAc), the identity of the molecule is in no doubt. Specifically, the rigid part of the complex with the fullerenes and the dinuclear cyclophane are well resolved. Several interesting details were revealed. The Pt^{II} coordination is square-planar, but with a significant deviation from the ideal

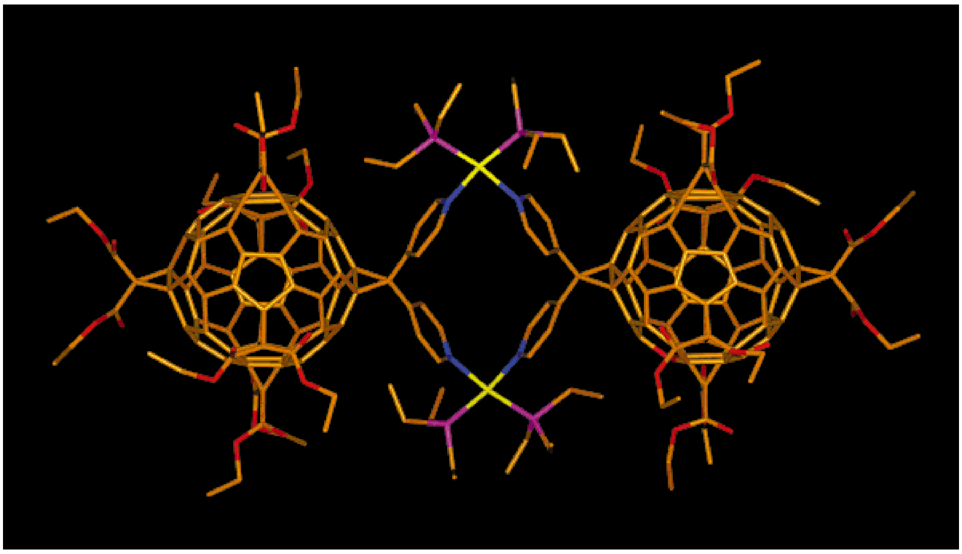


Figure 2. X-ray crystal structure of tetracationic **1**. The counteranions are omitted. C gold, Pt yellow, N blue, and P purple.

1433-7851/98/3713-1917 $ 17.50+.50/0

90° angles. The N-Pt-N angles are 81.6(3)°, whereas the P-Pt-P angle widens up to 97.2(2)°. The C(pyr)-C-C(pyr) angle of 113(2)° at the quaternary C atoms of the dipyridylmethano groups in **1** is identical to the angle seen in the X-ray crystal structure of ligand **2**.

The sum of the angles at the vertices of the macrocyclic parallelogram, measured at the two Pt atoms and the two quaternary C atoms of the dipyridylmethano groups is 390(5)° though 360° is needed for a perfectly planar assembly. In the reported X-ray structures of metal-assembled quadrangles, two situations are well documented: 1) The sum of the vertex angles is lower than the required value and the structures, in order to accommodate these smaller angles, adopt puckered conformations[8a] and 2) the sum of the angles fits this 360° requirement, and these structures typically show a perfectly planar macrocyclic conformation.[8b, e] An angular sum much larger then the ideal 360°, as observed for **1**, has, to the best of our knowledge, not been previously reported. In spite of an angular sum of 390(5)°, the assembly reported here is still planar; the maximum deviation of the two Pt^{II} centers, the quaternary C atoms, and the pyridine N and C_γ atoms from the best plane encompassing these centers is only 0.09 Å. The four pyridyl rings are nearly orthogonally oriented with respect to this plane: The maximum deviation of their best planes from perfect orthogonality is only 2°. As a result of the imperfect vertex angle sum, an outward bending of the edges in the parallelogram can be expected and, despite the moderate resolution of the structure, is actually observed. The Pt–P (2.26(1) Å) and the Pt–N (2.10(5) Å) bond lengths are normal. The cavity of the dinuclear cyclophane is small: the Pt–Pt distance is 10.26(3) Å and the distance between the quaternary C atoms only 7.42(6) Å, thus offering at best space for inclusion of an aliphatic chain.

Although the angles are not optimal for the synthesis of the macrocycle only one type of complex is formed, and oligomer formation was not observed at all. This result underlines the potential of this powerful metal-directed self-assembly to construct even more complex supermolecular fullerene arrays selectively: upon replacing further diethyl malonate addends in **2** with dipyridylmethano groups, larger assemblies such as rods or two- and three-dimensional fullerene networks should become accessible.

Experimental Section

1: To a solution of **2** (11 mg, 6.55×10^{-6} mol) in CD_2Cl_2 (1 mL) under Ar in the dark was added **7** (4.34 mg, 5.96×10^{-6} mol). The resulting mixture was stirred for 5 min until analysis by ^1H NMR spectroscopy showed complete complex formation. Recrystallization from EtOAc/CH_2Cl_2/PhH/Et_2O yielded **1** (13 mg, 91 %): yellow crystals; m.p. > 250 °C; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 271 (191 400), 282 (185 500), 318 (117 200), 337 (99 600), 437 (sh, 2700), 451 (sh, 1600); IR (KBr): $\tilde{\nu} = 1741\ cm^{-1}$ (C=O); 1153, 1111, 1027 (triflate); ^1H NMR (CD_2Cl_2, 300 MHz): $\delta = 1.13-1.42$ (m, 96 H); 1.78 (br. t, $J = 7.3$ Hz, 24 H); 4.23–4.46 (m, 40 H); 8.07 (d, $J = 6.6$ Hz, 8 H); 9.20 (br. d, 8 H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 8.03$, 14.26, 14.29, 14.35, 15.6–16.2 (m, CH_2P), 45.69, 46.26, 46.39, 46.81, 63.57, 63.67, 63.91, 69.47, 70.05 (2x), 70.26, 73.14, 131.08, 141.27, 141.82, 141.87, 141.93, 142.18, 143.03, 144.76, 145.93, 146.17, 146.22, 146.28, 146.82, 150.00, 152.29, 163.90, 164.06, 164.13 (2x); ^{19}F NMR (280 MHz, CD_2Cl_2): $\delta = -79.06$; ^{31}P NMR (120 MHz, CD_2Cl_2): $\delta = -4.56$ ($J_{Pt-P} = 3134$ Hz).

Received: February 12, 1998 [Z11469IE]
German version: *Angew. Chem.* **1998**, *110*, 2019–2022

Keywords: cyclophanes · fullerenes · N ligands · platinum · supramolecular chemistry

---

[1] a) C. A. Mirkin, W. B. Caldwell, *Tetrahedron* **1996**, *52*, 5113–5130; b) M. Prato, *J. Mater. Chem.* **1997**, *7*, 1097–1109; c) H. Imahori, Y. Sakata, *Adv. Mater.* **1997**, *9*, 537–546.

[2] a) F. Diederich, C. Dietrich-Buchecker, J.-F. Nierengarten, J.-P. Sauvage, *J. Chem. Soc. Chem. Commun.* **1995**, 781–782; b) N. Armaroli, F. Diederich, C. O. Dietrich Buchecker, L. Flamigni, G. Marconi, J.-F. Nierengarten, J.-P. Sauvage, *Chem. Eur. J.* **1998**, *4*, 406–416.

[3] P. R. Ashton, F. Diederich, M. Gómez-López, J.-F. Nierengarten, J. A. Preece, F. M. Raymo, J. F. Stoddart, *Angew. Chem.* **1997**, *109*, 1611–1614; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1448–1451.

[4] a) M. Maggini, A. Donò, G. Scorrano, M. Prato, *J: Chem. Soc. Chem. Commun.* **1995**, 845–846; b) D. Armspach, E. C. Constable, F. Diederich, C. E. Housecroft, J.-F. Nierengarten, *Chem. Commun.* **1996**, 2009–2010; c) D. Armspach, E. C. Constable, F. Diederich, C. E. Housecroft, J.-F. Nierengarten, *Chem. Eur. J.* **1998**, *4*, 723–733.

[5] a) J.-M. Lehn, *Supramolecular Chemistry—Concepts and Perspectives*, VCH, Weinheim, **1995**, pp. 139–197; b) J.-C. Chambron, C. O. Dietrich-Buchecker, J.-F. Nierengarten, J.-P. Sauvage, *Pure Appl. Chem.* **1994**, *66*, 1543–1550.

[6] a) M. Fujita, J. Yazaki, K. Ogura, *J. Am. Chem. Soc.* **1990**, *112*, 5645–5647; b) M. Fujita, S. Nagao, M. Iida, K. Ogata, K. Ogura, *J. Am. Chem. Soc.* **1993**, *115*, 1574–1576.

[7] For reviews on molecular squares see a) P. J. Stang, *Chem. Eur. J.* **1998**, *4*, 19–27; b) P. J. Stang, B. Olenyuk, *Acc. Chem. Res.* **1997**, *30*, 502–518.

[8] a) P. J. Stang, D. H. Cao, S. Saito, A. M. Arif, *J. Am. Chem. Soc.* **1995**, *117*, 6273–6283; b) P. J. Stang, K. Chen, A. M. Arif, *J. Am. Chem. Soc.* **1995**, *117*, 8793–8797; c) B. Olenyuk, J. A. Whiteford, P. J. Stang, *J. Am. Chem. Soc.* **1996**, *118*, 8221–8230; d) P. J. Stang, B. Olenyuk, J. Fan, A. M. Arif, *Organometallics* **1996**, *15*, 904–908; e) J. A. Whiteford, C. V. Lu, P. J. Stang, *J. Am. Chem. Soc.* **1997**, *119*, 2524–2533; f) P. J. Stang, D. H. Cao, K. Chen, G. M. Gray, D. C. Muddiman, R. D. Smith, *J. Am. Chem. Soc.* **1997**, *119*, 5163–5168.

[9] a) A. W. Schwabacher, J. Lee, H. Lei, *J. Am. Chem. Soc.* **1992**, *114*, 7597–7598; b) H. Rauter, E. C. Hillgeris, A. Erxleben, B. Lippert, *J. Am. Chem. Soc.* **1994**, *116*, 616–624; c) C. M. Drain, J.-M. Lehn, *J. Chem. Soc. Chem. Commun.* **1994**, 2313–2315; d) R. V. Slone, J. T. Hupp, C. L. Stern, T. E. Albrecht-Schmitt, *Inorg. Chem.* **1996**, *35*, 4096–4097.

[10] a) M. Fujita, S. Nagao, K. Ogura, *J. Am. Chem. Soc.* **1995**, *117*, 1649–1650; b) M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi, K. Ogura, *Nature* **1995**, *378*, 469–471; c) M. Fujita, M. Aoyagi, F. Ibukuro, K. Ogura, K. Yamaguchi, *J. Am. Chem. Soc.* **1998**, *120*, 611–612; d) P. J. Stang, B. Olenyuk, *Organometallics* **1997**, *16*, 3094–3096.

[11] F. L. Minn, C. L. Trichilo, C. R. Hurt, N. Filipescu, *J. Am. Chem. Soc.* **1970**, 92, 3600–3610.

[12] C. Bingel, *Chem. Ber.* **1993**, *126*, 1957–1959.

[13] All new compounds were fully characterized by ^1H and ^{13}C NMR, IR, and UV/Vis spectroscopies, FAB or MALDI-TOF-MS, and elemental analysis.

[14] For hexakis(methano)fullerenes, see a) L. Isaacs, R. F. Haldimann, F. Diederich, *Angew, Chem.* **1994**, *106*, 2434–2437; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2339–2342; b) P. Seiler, L. Isaacs, F. Diederich, *Helv. Chim. Acta* **1996**, *79*, 1047–1058; c) L. Isaacs, F. Diederich, R. F. Haldimann, *Helv. Chim. Acta* **1997**, *80*, 317–342; d) A. Hirsch, I. Lamparth, T. Grösser, H. R. Karfunkel, *J. Am. Chem. Soc.* **1994**, *116*, 9385–9386; e) I. Lamparth, A. Herzog, A. Hirsch, *Tetrahedron* **1996**, *52*, 5065–5075.

[15] a) I. Lamparth, C. Maichle-Mössmer, A. Hirsch, *Angew. Chem.* **1995**, *107*, 1755–1757; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1607–1609; b) X. Camps, H. Schönberger, A. Hirsch, *Chem. Eur. J.* **1997**, *3*, 561–567; c) P. Timmerman, L. E. Witschel, F. Diederich, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Helv. Chim. Acta* **1996**, *79*, 6–20.

[16] a) X-ray crystal data for **2**:[16c] Yellow plate-like crystals ($0.5 \times 0.4 \times 0.3$ mm) were obtained by slow diffusion of hexane into a solution of **2** in CH_2Cl_2/EtOAc/PhH and contained one benzene molecule and

partially resolved EtOAc molecules ($C_{120.75}H_{64}N_2O_{20}$, $M_r = 1862.74$): Triclinic space group $P\bar{1}$, $Z = 4$, $\rho_{calcd} = 1.368\,g\,cm^{-3}$, $a = 14.218(7)$, $b = 25.562(13)$, $c = 25.916(13)$ Å, $\alpha = 84.18(3)$, $\beta = 74.84(3)$, $\gamma = 89.81(4)°$, $V = 9042(8)$ Å^3. The structure was solved starting with a single fullerene oriented by PATTSEE orientation search and subsequent tangent expansion in $P1$. Refinement by full-matrix least-squares analysis (SHELXTL PLUS; heavy atoms anisotropic, H atoms fixed, whereby H positions are based on stereochemical considerations) to give $R(1) = 0.0964$ and $R_w(2) = 0.2564$ for 2554 variables, 756 restraints, and 18545 observed reflections with $I > 2\sigma(I)$ and $1.74 \leq \theta \leq 50.01$. b) X-ray crystal data for **1**:[16c] Yellow rhomboid crystals ($0.1 \times 0.1 \times 0.015$ mm) were obtained by slow diffusion of hexane into a solution of **1** in EtOAc/PhH and contained a large amount of unresolved solvent molecules ($C_{200.5}H_5N_2O_{20}P_2PtS$, $M_r = 3050.16$): Monoclinic space group $P2(1)/c$, $Z = 4$, $\rho_{calcd} = 1.580\,g\,cm^{-3}$, $a = 29.17(2)$, $b = 17.986(9)$, $c = 27.37(2)$ Å, $\alpha = 90$, $\beta = 116.75(5)$, $\gamma = 90°$, $V = 12821(13)$ Å^3. The structure was solved by Patterson methods and refined by full-matrix least-squares analysis (SHELXTL PLUS; heavy atoms isotropic, bond distances and angles of the partially disordered diethyl malonate groups constrained by SHELX-DFIX-instructions) to give $R = 0.109$ and $R_w = 0.092$ (based on F) for 756 variables and 5549 observed reflections with $I > 2\sigma(I)$ and $1.70 \leq \theta \leq 35.10$. c) Data collection at $T = 293$ K: Picker–Stoe diffractometer, $Cu_{K\alpha}$ radiation using ω scans, $\lambda = 1.54178$ Å. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101112. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

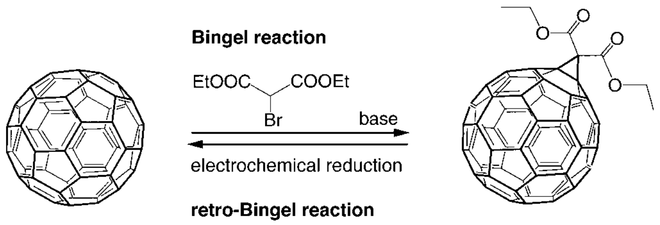
[17] F. Cardullo, P. Seiler, L. Isaacs, J.-F. Nierengarten, R. F. Haldimann, F. Diederich, T. Mordasini-Denti, W. Thiel, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Helv. Chim. Acta* **1997**, *80*, 343–371.

Preparation of Enantiomerically Pure C_{76} with a General Electrochemical Method for the Removal of Di(alkoxycarbonyl)methano Bridges from Methanofullerenes: The Retro-Bingel Reaction**

Roland Kessinger, Jeanne Crassous, Andreas Herrmann, Markus Rüttimann, Luis Echegoyen,* and François Diederich*.

Since its discovery in 1993, the Bingel reaction[1] has been widely used as a mild, versatile method to introduce one or more methano bridges into C_{60}[2] and the higher fullerenes.[3] Cyclopropanation of a fullerene, according to the original Bingel protocol, occurs by treating the carbon allotrope with 2-bromomalonate esters in the presence of base. Modified procedures allowing in situ formation of the 2-bromo- or 2-iodomalonates have also been reported.[4, 5] Cyclopropane rings fused to fullerenes are highly stable and cannot be removed thermally or by wet-chemical methods, although mass spectrometric fragmentation occurs rather readily.[6]

The majority of methanofullerenes are also known to be very stable under the conditions of cyclic (CV) and steady-state voltammetry (SSV).[7] A notable exception was reported by Haddon, Wudl, and co-workers[8] for the monoanion of 1,2-methano[60]fullerene-61,61-dinitrile, which was unstable under CV conditions and, based upon voltammetric observations, was reported to revert back to C_{60}.[9] Also, the electrochemistry group of M. Gross at Strasbourg had noted a decomposition of dianions of specific bis(methano)fullerenes with a *cis-2* addition pattern during CV and SSV, and this observation provided the impetus for the work reported here.[7c, 10] In this paper, we describe the retro-Bingel reaction (Scheme 1) as a general, preparative electrochemical method[11, 12] for the removal of di(alkoxycarbonyl)methano bridges from methanofullerenes and illustrate its power with the preparation of the pure enantiomers of C_{76}.[13, 14]



1

Scheme 1. The Bingel and retro-Bingel reactions.

Electrochemical investigations on diethyl 1,2-methano[60]-fullerene-61,61-dicarboxylate (**1**) and similar C_{60} monoadducts have shown that the first two reduction steps are electrochemically and chemically reversible on the voltammetric time scale at a scan rate of $100\,mV\,s^{-1}$.[7b, 8] Our CV data are in agreement with these earlier findings (Figure 1). Chemical irreversibility of the second reduction is only evident at very slow scan rates. We reduced **1** electrochemically in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 at 293 K at controlled potential, initially to its monoanionic state (at −1.2 V versus a Ag wire pseudo reference electrode).[15] The charge transferred corresponded exactly to one electron per molecule, and the resulting anion was very stable under these conditions, with no apparent decomposition after 30 min. The formation of the dianion (at −1.55 V versus Ag) by controlled potential electrolysis (CPE, Figure 1), on the other hand, was surprising, because the charge transferred corresponded to four electrons per molecule and not just one. Clear changes in the CV indicated that some chemical reaction had taken place. After 30 min of electrolysis, reoxidation of the solution at 0 V (versus Ag), followed by column chromatography (SiO_2, toluene) yielded pure C_{60} in over 80% yield (Table 1). It must be stressed that the two first reduction steps are perfectly reversible on the CV time scale at a scan rate of

---

[*] Prof. Dr. L. Echegoyen
Department of Chemistry, University of Miami
Coral Gables, FL 33124, USA
Fax: (+1)305-284-4571
E-mail: lechegoyen@umiami.ir.miami.edu

Prof. Dr. F. Diederich, Dr. J. Crassous, Dr. A. Herrmann,
Dipl.-Chem. R. Kessinger, Dipl.-Chem. M. Rüttimann
Laboratorium für Organische Chemie, ETH-Zentrum
Universitätstrasse 16, CH-8092 Zürich (Switzerland)
Fax: (+41)1-632-1109
E-mail: diederich@org.chem.ethz.ch

[**] This work was supported by the Swiss National Science Foundation, the US National Science Foundation (CHE-9313018), an NIH Fogarty Fellowship (1 F06 TW-02231-01 to L.E.), and Hoechst AG.

1433-7851/98/3713-1919 $ 17.50+.50/0