

26. Multiple Adducts of C₆₀ by Tether-Directed Remote Functionalization and Synthesis of Soluble Derivatives of New Carbon Allotropes C_{n(60+5)}

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A comprehensive series of multiple adducts of C₆₀ was prepared by tether-directed remote functionalization. When the tether-reactive-group conjugates **2** and **10** were attached to methano[60]fullerenecarboxylic acid (= cyclopropafullerene-C₆₀-I_n-carboxylic acid) and C₆₀, respectively, the *e*-bis-adducts **4** and **9** (Schemes 1 and 2) were obtained with complete regioselectivity as predicted by semi-empirical PM3 calculations (Fig. 2). Attachment of the anchor-tether-reactive-group conjugate **13** to C₆₀ by *Bingel* reaction, followed by double intramolecular *Diels-Alder* cycloaddition afforded the tris-adduct **12** (Scheme 3). Starting from **12**, a series of selective *e*-additions led to the tetrakis-adducts **16** and **19** (Scheme 4), pentakis-adducts **20–23** (Scheme 5), and, ultimately, to hexakis-adducts **24** and **25** (Scheme 6), and **29** and **30** (Scheme 7) with a pseudo-octahedral addition pattern on the fullerene core. Oxidative cyclization of diethynylmethanofullerene **30** under *Eglinton-Glaser* conditions afforded the trimeric and tetrameric acetylenic macrocycles **26**, with three, and **27**, with four appended C₆₀ moieties, respectively (Scheme 8). These multinanometer-sized compounds are the first soluble derivatives of C₁₉₅ and C₂₆₀, two members of a new class of fullerene-acetylene hybrid C-allotropes with the general formula C_{n(60+5)}. The matrix-assisted laser-desorption time-of-flight mass spectra of **26** and **27** showed a remarkable fragmentation; the sequential loss of fullerene spheres led to the formation of ions corresponding to mono-fullerene adducts of the cyclocarbons *cyclo*-C₁₅ and *cyclo*-C₂₀ (Fig. 4). Large solvent effects were observed in the *Bingel* addition of 2-bromomalonates to higher adducts of C₆₀, with the use of polar solvents enhancing the reaction rate without loss of regioselectivity. Experimental evidence for the enhanced reactivity of *e*_{face} over *e*_{edge} bonds was obtained, which had previously been predicted in computational studies. The correlated series of mono- to hexakis-adducts of C₆₀ allowed identification of the changes in reactivity and physical properties that occur, when the conjugated π -electron chromophore of the fullerene is reduced as a result of increasing functionalization; this analysis is the subject of the directly following paper.

1. Introduction. – A rich variety of methods for the preparation of covalent mono-adducts of buckminsterfullerene C₆₀ was developed in many laboratories worldwide [1–4] after the seminal discovery of a bulk fullerene preparation method by *Krättschmer*, *Huffman*, and coworkers in 1990 [5]. Subsequently, the regiospecific formation of covalent poly-adducts became the frontier in the exploration of the chemistry of the new molecular allotrope of carbon. Monofunctionalized C₆₀ possesses nine different 6-6 bonds (bonds at the junction between two six-membered rings) that can react in a second addition, and a widely accepted nomenclature to describe the various sites of second attack was introduced by *Hirsch* and coworkers [6] (Fig. 1). Similar problems of isomer formation arise in the attack by a third addend to a purified bis-adduct as well as in the formation of more highly functionalized fullerenes.

Multiple regioisomer formation is reduced in reversible reactions with transition metal complexes [7] or halogens [8], which yield the thermodynamically most stable isomer or an isomer that crystallizes from the reaction mixture. Alternatively, mixtures

of many possible multiple adducts were produced by successive, irreversible reactions at the C_{60} sphere, and purification was subsequently accomplished by often tedious chromatographic separations or by recrystallization, if possible [6] [9].

In 1993, we became interested in developing a more rational approach to the production of a single, desired regioisomer in multiple-functionalization reactions. Our ultimate objective was to provide selective access to tailor-made multiple adducts of C_{60} with any desirable functionalization pattern for potential future use as novel three-dimensional building blocks in the construction of advanced materials and in biomedical applications. Furthermore, we hoped to identify the changes in reactivity and physical properties which occur when the conjugated π -electron chromophore of the fullerene is reduced as a result of increasing functionalization. To achieve regioselective multiple additions, we applied the concept of tether-directed remote functionalization (*Fig. 1*), which had been developed by *Breslow* [10] for the regioselective derivatization of steroids and long-chain alkanes. A great variety of fullerene multiple adducts has now been prepared in our group by this methodology which is described in detail in this paper [11–14].

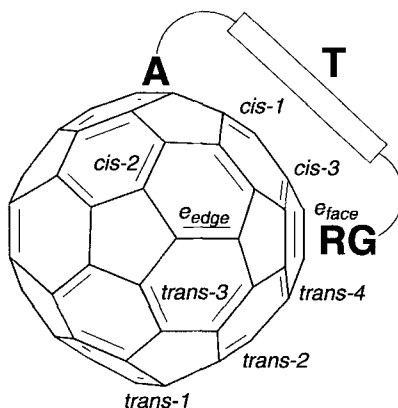


Fig. 1. Naming of the bis-addition patterns, relative to the 'anchor' mono-adduct, according to Hirsch and coworkers [6] and schematic representation of the tether-directed remote bis-functionalization of C_{60} . A = anchor, T = tether, RG = reactive group. The e_{face} bond sees the face of the anchor A whereas the e_{edge} bond sees its edge.

Several other protocols, some of which also rely on tether control [15], have in the meanwhile been applied to the regioselective multiple functionalization of C_{60} . We recently described a new tether-controlled remote functionalization which, upon application of chiral tethers, permitted the enantioselective preparation of optically active bis-adducts whose chirality resulted exclusively from the addition pattern [16]. Various groups reported the regioselective formation of 'diazafulleroids' with N-atoms bridging two adjacent open 6-5 bonds (at the junction of a six- and a five-membered ring) of the carbon sphere [17]. An elegant, topochemically controlled solid-state reaction provided access to a *trans-1* bis-adduct of C_{60} [18]. Hexakis-adducts of C_{60} , with a pseudo-octahedral addition pattern (see below), were prepared directly from C_{60} or from mono-adducts with [19] [20] or without [21] assistance by a reversible template. A reversible template was also used to control the regiochemistry of bis-additions [22].

In this paper, we give a full account on our versatile, tether-directed remote functionalization method which allowed for the first time the regioselective formation of a

complete series of bis- to hexakis-adducts of C_{60} [11–13]. All compounds were isolated in pure form without the application of HPLC methods. Subsequently, we describe the formation of soluble derivatives of C_{195} and C_{260} , two members of a new class of fullerene-acetylene hybrid carbon allotropes [20] [23] with the general molecular formula $C_{n(60+5)}$. The directly following paper [24] reports an important extension of the new methodology which allows removal of the tether-reactive-group conjugate under formation of another series of multiple adducts that are not accessible by stepwise additions. The second paper also provides an in-depth analysis of the changes in chemical reactivity and physical properties that occur when the conjugated fullerene π -chromophore is reduced in a specific way as a result of increasing functionalization.

2. Results and Discussion. – 2.1. *Design of the Anchor/Tether-Reactive-Group Conjugate.* We first targeted the selective formation of an equatorial bis-adduct of C_{60} starting from methano[60]fullerenecarboxylic acid (= cyclopropa fullerene- C_{60} - I_h -carboxylic acid; **1**) [25] as the anchor (see below, *Scheme 1*). As the reactive group, we chose a 2-substituted buta-1,3-diene known to undergo irreversible *Diels-Alder* reactions with C_{60} at 6-6 bonds [26] [27]. The selection of the correct tether between anchor and reactive group was critical for the regioselectivity of the intramolecular *Diels-Alder* addition. It should favor attack at the e_{face} bond (*Fig. 1*) over attack at the second equatorial e_{edge} or the *cis*-3 and *trans*-4 bonds near the equator. We selected the 4-substituted benzyl alcohol **2** as tether reactive-group conjugate since molecular-model examinations suggested that mono-adduct **3**, in which conjugate **2** had been attached to anchor **1**, would readily differentiate between the desired position of attack (e_{face}) and the e_{edge} and *trans*-4 bonds. A PM3 computational study [28] finally predicted that **3** would also lead to a large preference for the targeted e_{face} bis-adduct **4** over the *cis*-3 regioisomer **5** (*Fig. 2*). The heat of formation of **4** was calculated to be $6.5 \text{ kcal mol}^{-1}$ lower than that of the lowest-energy conformer of **5**. A closer examination of the calculated geometry of **5** showed that the tether was

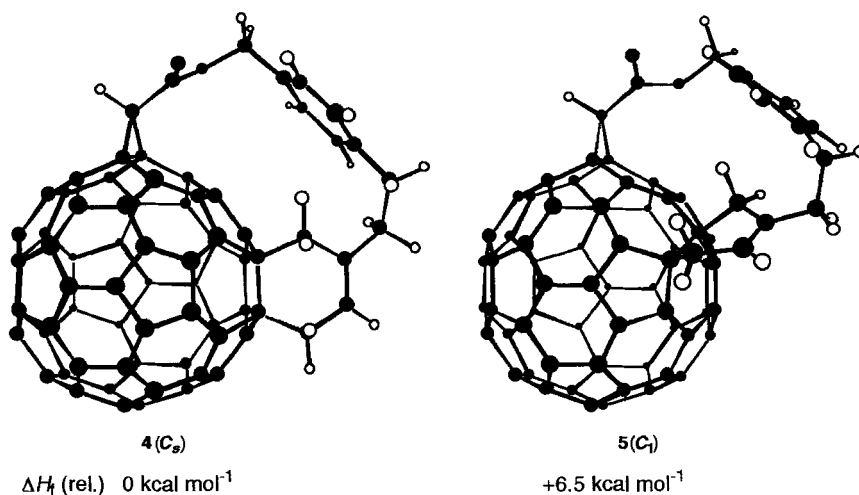
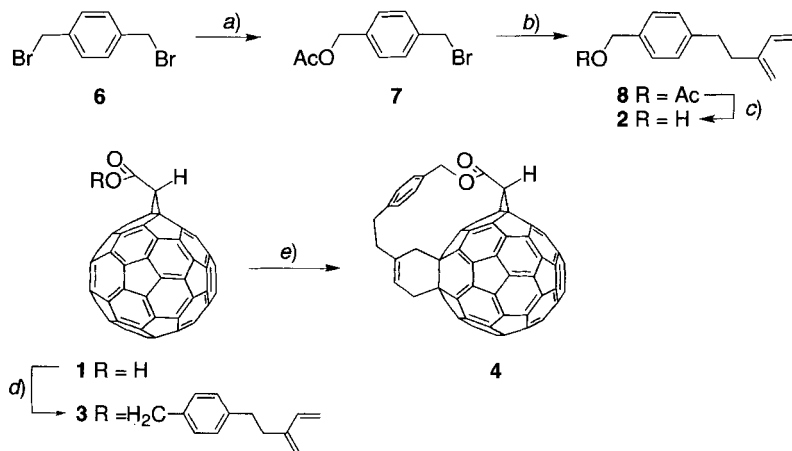


Fig. 2. PM3-Calculated structures and heats of formation for the two possible regioisomeric bis-adducts **4** and **5**

too short in the conformer shown and too long in the higher-energy conformer in which the double bond of the cyclohexene boat is oriented towards the anchor. This mismatch of the tether length in **5** leads to distortions in the bridging benzene ring and also to skewing of the ester group, which both increase the heat of formation. Experimentally, the different symmetries of **4** (C_s) and **5** (C_1) were expected to allow facile identification of the bis-adduct formed by ^{13}C -NMR spectroscopy.

2.2. Synthesis of Bis-adducts of C_{60} . The synthesis of the tether-reactive-group conjugate **2** (Scheme 1) started from α,α' -dibromo-*p*-xylene (**6**) which was transformed into the acetoxy derivative **7**. Formation of the benzylic zinc organometallic [29], followed by transmetallation to the cyanocuprate and reaction with 2-(bromomethyl)buta-1,3-diene [30] gave **8** which was deprotected to yield **2**. Coupling of **2** to anchor **1** via esterification proceeded smoothly in the presence of dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HOBt), and 4-(dimethylamino)pyridine (DMAP) and afforded the intermediate wine-red methanofullerene **3** which was purified by flash chromatography (SiO_2 , PhMe/hexane 2:1). Characterization of **3** was limited to UV/VIS spectroscopy which showed the two diagnostic absorption bands of a mono-adduct at λ_{max} 429 and 692 nm [31 a]. Further characterization was not attempted due to rapid polymerization of **3** upon evaporation to dryness, presumably through intermolecular *Diels-Alder* reaction.

Scheme 1. Synthesis of Bis-adduct **4**



a) KOAc, [18]crown-6, MeCN, r.t.; 47%. b) Zn, THF, 5°; then CuCN, LiCl, THF, -75°; then 2-(bromomethyl)buta-1,3-diene, -75 → 20°; 61%. c) K_2CO_3 , MeOH, r.t.; 96%. d) DCC, HOBt, DMAP, PhBr, r.t. e) PhMe, 80°, 44 h; 23%.

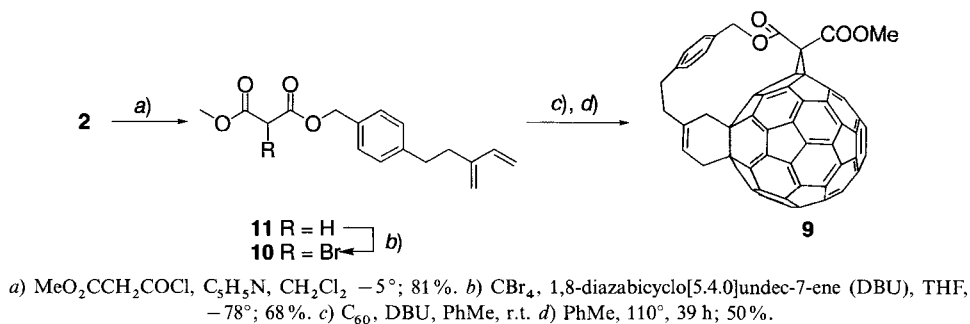
When a *ca.* 0.1M solution of **3** in PhMe was heated for 44 h to 80°, a color change from wine-red to orange-brown occurred, and subsequent flash chromatographic workup and recrystallization gave bis-adduct **4** in 23% yield. The compound was poorly soluble in PhMe or CHCl_3 , but sufficient solubility in CS_2 allowed its complete spectroscopic characterization. Unambiguous evidence for formation of C_s -symmetrical **4** was obtained by ^1H - and ^{13}C -NMR spectroscopy. The ^1H -NMR spectrum did not show any diastereotopic methylene protons which strongly suggested molecular C_s -symmetry on

the NMR time scale with the two boat forms of the cyclohexene ring [26a] [31] and the rotamers formed by rotation about the ester group rapidly interconverting. The presence of 32 resonances for the fullerene C-atoms demonstrated conclusively that the intramolecular *Diels-Alder* reaction had occurred at the e_{face} -6-6 bond to give C_s -symmetrical **4**.

Cyclohexene rings fused to C_{60} such as those formed by *Diels-Alder* cycloaddition were shown by Rubin and coworkers [32] to rapidly undergo a 1O_2 -ene reaction in the presence of light and O_2 , with the fullerene derivative acting as a photosensitizer for the formation of 1O_2 [9d] [33]. This reaction also caused rapid decomposition of **4** as well as of most of the other higher adducts described in the following and, therefore, these compounds must be handled with extreme caution with exclusion of light and air. In the solid state under Ar at 0° in the dark, however, **4** is stable for extended periods of time. One other fullerene product (ca. 5% yield) was also present in the reaction mixture, but matrix-assisted laser-desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-MS) showed it to be a by-product due to oxidation of **4** rather than a regioisomeric bis-adduct. The isomeric bis-adduct **5** was not detected in the reaction mixture. The rather low isolated yield of **4** is a reflection of the difficulties encountered with its chromatographic separation from its oxidation product.

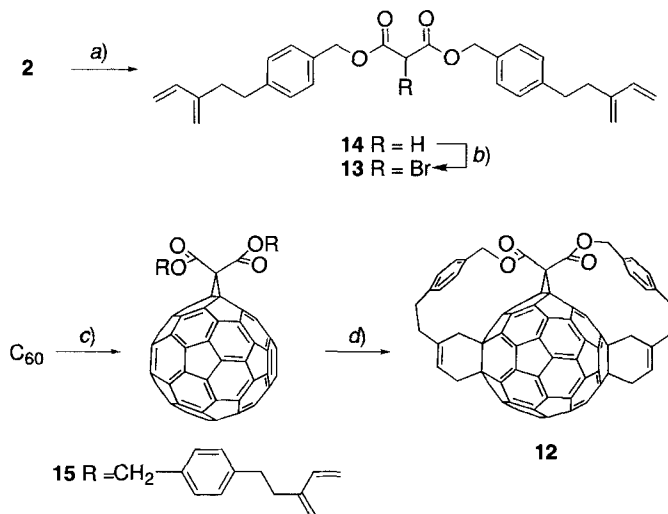
Since bis-adduct **4** was too insoluble for electrochemical studies in CH_2Cl_2 [13], we prepared the more soluble derivative **9** by tether-directed remote functionalization. For the synthesis of the anchor/tether-reactive-group conjugate **10**, benzyl alcohol **2** was esterified with 'methyl malonyl chloride' (MeO_2CCH_2COCl) to give **11**, followed by bromination (*Scheme 2*). Attachment of **10** to C_{60} in a *Bingel* reaction [34], followed by heating the wine-red mono-adduct in refluxing PhMe for 39 h to complete the intramolecular *Diels-Alder* addition, afforded **9** in 50% yield as a CH_2Cl_2 -soluble brown solid which was isolated by flash chromatography. The spectral data for **9** were almost identical to those recorded for **4**, which supported the proposed C_s -symmetrical structure.

Scheme 2. Synthesis of Bis-adduct **9**



2.3. Synthesis of Tris-adduct 12. For the regiospecific formation of tris-adduct **12**, resulting from double *Diels-Alder* addition to the two e_{face} -6-6 bonds in relation to the anchor, the doubly tethered precursor **13** was prepared by reacting malonyl dichloride with **2** (2 equiv.) to give **14**, followed by bromination (*Scheme 3*). *Bingel* addition of **13** to C_{60} afforded the wine-red methanofullerene **15** which was separated by flash chro-

matography from excess C_{60} . The identity of **15** was established by $^1\text{H-NMR}$ and UV/VIS spectroscopy. The $^1\text{H-NMR}$ spectrum showed all expected resonances for tether and reactive groups, and the electronic absorption spectrum displayed the two diagnostic mono-adduct bands [31 a] at λ_{max} 429 and 690 nm. Heating a solution of **15** (*ca.* 0.6 mM) in PhMe to 110° for 36 h resulted in a color change from wine-red to brown-orange, and subsequent flash chromatography provided C_{2v} -symmetrical **12** in 60% yield (based on conjugate **13**). By this method, gram-quantities of tris-adduct became readily accessible in single runs.

Scheme 3. Synthesis of Tris-adduct **12**

a) $\text{ClCOCH}_2\text{COCl}$, $\text{C}_5\text{H}_5\text{N}$, CH_2Cl_2 , 0° ; 80%. b) CBr_4 , DBU, THF, -78° ; 79%. c) **13**, DBU, PhMe, r.t.
d) PhMe, 110° , 39 h; 60%.

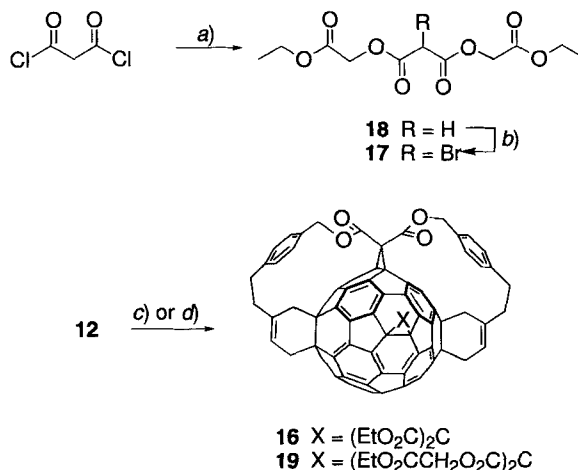
Tris-adduct **12** was poorly soluble in PhMe, CS_2 , and CHCl_3 , but reasonably soluble in Cl_2CDCl_2 , which allowed its complete characterization. The $^1\text{H-NMR}$ spectrum of **12** closely resembled that of **4**, minus the resonance for the proton of the methano moiety. The $^{13}\text{C-NMR}$ spectrum showed the expected 17 resonances for the fullerene C-atoms in a C_{2v} -symmetrical molecule. Tris-adduct **12** appeared to be less sensitive to light and O_2 than bis-adduct **4** which could be due to a reduced ability of the higher adduct to photosensitize the formation of $^1\text{O}_2$; however, it was still necessary to work with as little exposure to light and air as possible.

2.4. *Synthesis of Tetrakis-adducts of C_{60} .* The regioselectivity observed by Hirsch and coworkers in the formation of an *e,e,e*-tris-adduct (all addends are in an equatorial relation to each other) starting from an *e*-bis-adduct [6] raised our optimism that further functionalization of **12** would lead to regioisomerically pure tetrakis- and even higher adducts. We first tested the reactivity of our tris-adduct in comparison to C_{60} . Upon treatment of **12** with an excess of anthracene (12 equiv.) in $\text{Cl}_2\text{CHCHCl}_2$ at 65° , no color change was noted within 19 h, whereas C_{60} readily underwent a *Diels-Alder* addition under these conditions [9 d] [35]. In a second test, a solution of **12** in PhCl was treated

with an excess of 2,5-dihydro-2,2-dimethoxy-5,5-dimethyl-1,3,4-oxadiazole (10 equiv.), which generates dimethoxycarbene at elevated temperatures [36]. Whereas C_{60} readily formed 61,61-dimethoxymethano[60]fullerene under these conditions [37] [38], no reaction was observed with **12** (TLC). Clearly, threefold functionalization significantly reduces the chemical reactivity of **12** as compared to free C_{60} .

In contrast, the *Bingel* addition of diethyl 2-bromomalonate (5 equiv.) to **12** in PhCl at room temperature in the presence of DBU (5 equiv.) was successful and yielded tetrakis-adduct **16** as a bright-red solid in 72% yield (*Scheme 4*). The C_s -symmetrical structure, resulting from regioselective addition of the malonate to a 6-6 bond which is equatorial to all three previously introduced addends, was proven by 1H - and ^{13}C -NMR spectroscopy. Specifically, the 1H -NMR spectrum showed two sets of signals for the diastereotopic CH_2 protons in the cyclohexene rings as well as two chemically nonequivalent ethyl groups. The ^{13}C -NMR spectrum displayed 32 resonances for the fullerene core C-atoms, which conclusively established C_s symmetry. Compound **16** is the only possible tetrakis-adduct with this symmetry that can be prepared starting from **12**; all other regioisomers are either C_{2v} - or C_1 -symmetrical. The tetrakis-adduct is thermally robust and showed no sign of melting or decomposition below 270° ; in contrast to its precursor molecules, it is highly soluble in $CHCl_3$.

Scheme 4. Synthesis of Tetrakis-adducts **16** and **19**



a) $HOCH_2COOEt$, C_5H_5N , CH_2Cl_2 , 0° ; 73%. b) CBr_4 , DBU, THF, -70° ; 75%. c) $(EtO_2C)_2CHBr$ (5 equiv.), DBU (5 equiv.), PhCl, r.t.; 72%. d) **17** (7.5 equiv.), DBU (7.5 equiv.), PhCl, r.t.; 70%. The two newly formed benzenoid ring substructures in **16** and **19** are highlighted in bold.

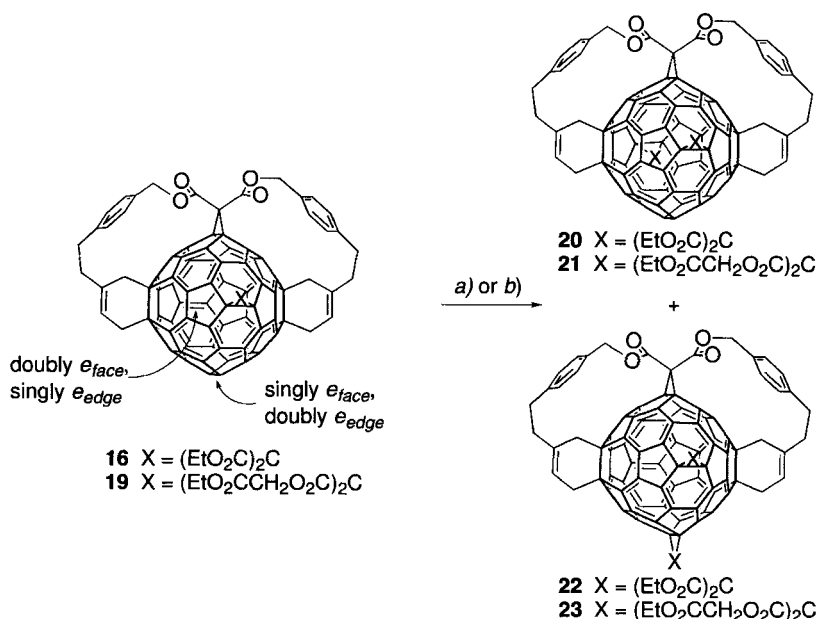
No isomeric tetrakis-adducts were detected by TLC or 1H -NMR spectroscopy. This high selectivity is in accord with the computational studies by Hirsch and coworkers [9e] who showed that the orbital coefficients in the LUMO, which apparently control kinetic-product formation, are enhanced at *e*-bonds (as well as at *trans*-3 and *cis*-2 bonds). The transition states of the addition leading to **16** might be further lowered in energy by the generation of two isolated benzenoid rings as shown in *Scheme 4*; additions to any other 6-6 bonds in **12** fail to generate such benzenoid ring substructures.

To facilitate the separation of regioisomeric pentakis-adducts (see below), bis(2-ethoxy-2-oxoethyl) 2-bromomalonate (**17**) with significantly more R_f -determining ester groups than those in the corresponding diethyl ester was reacted with tris-adduct **12**. Compound **17** was prepared in two steps from malonyl dichloride via **18** (Scheme 4). Thus, reaction of **12** with a large excess of **17** (7.5 equiv.) and DBU (7.5 equiv.) at room temperature in PhCl provided unreacted starting material, tetrakis-adducts, and some pentakis-adduct, which were separated chromatographically (SiO_2 - H , CH_2Cl_2). The major product (70%) was the expected C_s -symmetrical tetrakis-adduct **19** which was separated from three other minor tetrakis-adducts resulting presumably from addition to less activated 6-6 bonds. The lower selectivity observed in the formation of **19**, as compared to **16**, is presumably due to increased steric interactions of the bulkier new addend with the three ones already in place, which offset the intrinsic electronic preferences of the system. Tetrakis-adduct **19** showed excellent solubility in CHCl_3 , PhCl, THF, and even Me_2SO ; it can be precipitated by addition of cyclohexane in which it is insoluble.

2.5. Synthesis of Pentakis-adducts of C_{60} : Solvent Effects in the Bingel Reaction and e_{face} vs. e_{edge} Directing Effects. When tetrakis-adduct **16** was reacted with diethyl 2-bromomalonate (5 equiv.) and DBU (5 equiv.) in PhCl at room temperature, a mixture of the orange-colored pentakis-adducts **20** and **22** was obtained in a total yield of 70% (Scheme 5). The ratio **20/22** was determined as 8:2 by integration of the benzylic CH_2 ^1H -NMR signals at 5.1 and 5.3 ppm, respectively. The initial assignment of a C_{2v} -symmetrical structure to **20** and a C_s -symmetrical structure to **22** was based on the ^1H -NMR spectrum of the isomeric mixture which showed a d and a s for the CH_2 protons of the cyclohexene moieties in **20**, whereas these protons are diastereotopic in **22** and gave the expected coupling patterns. Repeated recrystallization out of CHCl_3 /hexane gave **20** with a maximum isomeric purity of only 96%. The preparative scale column-chromatographic separation (SiO_2 - H) of **20** and **22** was very tedious; only regioisomer **20** could be isolated in pure form (33% yield) from reactions of **16** with a 7.5-fold excess of diethyl 2-bromomalonate and DBU. These separation problems are due to extremely similar retention factors of the two regioisomers, resulting from the almost identical orientation of their three R_f -determining malonate addends on the fullerene surface. The three malonate residues in each case are *trans*-1,*e,e*-related, differing only in the choice of the two nonequivalent *e*-bonds. The ^{13}C -NMR spectrum of pure **20** fully confirmed its high symmetry, showing all 17 core resonances expected for a C_{2v} -symmetrical fullerene derivative.

We explored the solvent and temperature dependency of the *Bingel* reaction in the preparation of the pentakis-adducts in order to possibly increase the regioselectivity. When the addition was conducted in CH_2Cl_2 at -40° , the ratio **20/22** was 75:25. In contrast, when the reaction was conducted in CCl_4 at room temperature, a much higher selectivity of 91:9 was observed. Use of a less polar solvent such as cyclohexane, which presumably would have given a further enhanced regioselectivity, was not possible for solubility reasons.

The regioselectivity observed for attack at one triply *e*-6-6 bond, leading to **20**, over attack at another triply *e*-6-6 bond, leading to **22**, was actually quite remarkable. Close examination of the molecular structure of tetrakis-adduct **16** revealed that the more reactive bond is doubly e_{face} and singly e_{edge} (Fig. 1, Scheme 5), whereas the less reactive 6-6 bond is doubly e_{edge} and once e_{face} with regard to the addends already in place. This

Scheme 5. Synthesis of Pentakis-adducts **20–23**

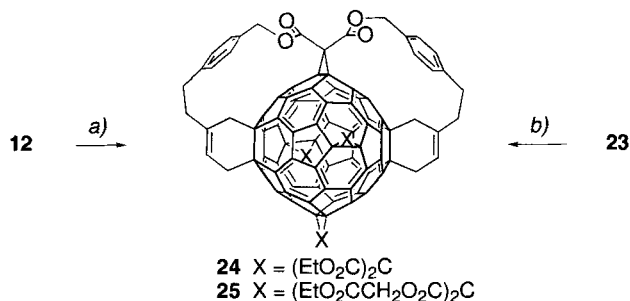
a) $(\text{EtO}_2\text{C})_2\text{CHBr}$ (5 equiv.), DBU (7.5 equiv.), PhCl, r.t.; 33% (**20**). b) **17** (1 equiv.), DBU (1 equiv.) PhCl, r.t.; 28% (**21**), 11% (**23**), 31% (recovered **19**).

can be considered as the first experimental evidence for the enhanced reactivity of e_{face} bonds over e_{edge} bonds, which had previously been predicted in computational studies by Hirsch and coworkers [9e].

A complete separation of the formed pentakis-adducts was possible if the fourth and fifth addends were bis(2-ethoxy-2-oxoethyl)malonates which generate larger differences in the R_f values. When tetrakis-adduct **19** was reacted with **17** (1 equiv.) and DBU (1 equiv.) in PhCl at room temperature, chromatographic workup (SiO_2 - H , $\text{CH}_2\text{Cl}_2/\text{AcOEt}$ 100:1.5) afforded isomerically pure C_{2v} -pentakis-adduct **21** (28%) and C_s -pentakis-adduct **23** (11%) (isomer ratio 72:28; Scheme 5), along with trace quantities of a third product. The colors and, accordingly, the UV/VIS spectra [24] of **21** and **23** are remarkably different: whereas a solution of **21** in CH_2Cl_2 is pale-orange, the corresponding solution of **23** is orange-red. The ^{13}C -NMR spectrum of **23** displayed 30 of the 32 resonances expected for the fullerene core in a C_s -symmetrical adduct.

2.6. Synthesis of Hexakis-adducts of C_{60} . When a suspension of tris-adduct **12** was treated with diethyl 2-bromomalonate (10 equiv.) and DBU (10 equiv.) at room temperature in dry PhCl, the mixture became rapidly homogeneous, and, after 2 h, flash-chromatographic workup yielded the bright-yellow hexakis-adduct **24** in 73% yield (Scheme 6). Compound **24** possesses a pseudo-octahedral e,e,e,e,e,e -addition pattern similar to other hexakis-adducts described in the literature [7a] [9e] [19–21] and was formed with complete regioselectivity. Its structure was conclusively demonstrated by X-ray crystallography [12] [39]. In solution, the compound has averaged C_{2v} -symmetry

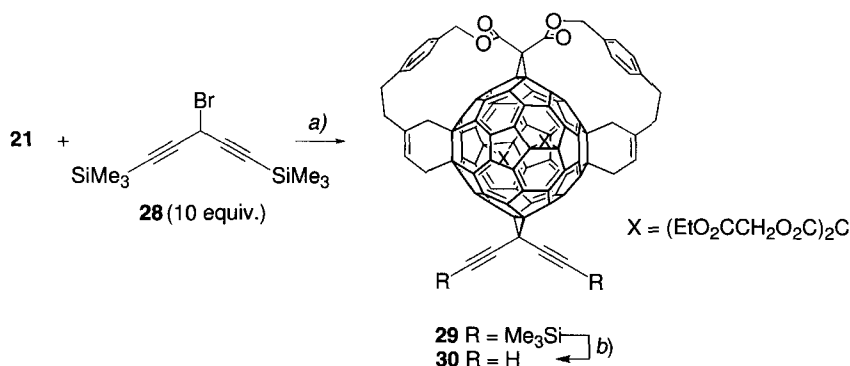
as revealed by the presence of 16 of the 17 expected resonances for fullerene C-atoms and three nonequivalent CO₂Et groups in its ¹³C-NMR spectrum. Hexakis-adduct **24** is highly soluble and dissolves readily in chlorinated and aromatic solvents; more than 40 mg can be dissolved in 1 ml of CHCl₃. It is a thermally robust solid which showed no sign of decomposition or melting up to 270° and is significantly more stable to light and air than the mono- to pentakis-adducts described above. Apparently, hexakis-adducts are no longer able to efficiently photosensitize the formation of ¹O₂, which would undergo destructive ¹O₂-ene reaction at the cyclohexene moieties, as discussed above (Sect. 2.2). The high regioselectivity observed in the formation of **24** can be attributed to the preference for additions at *e*-bonds due to enhanced LUMO coefficients at these 6-6 bonds [9e] and to the generation of a 'cubic' cyclophane substructure [13] with eight stable benzenoid rings which, in the X-ray crystal structure, show reduced bond length alteration [39]. Formation of the stable benzenoid structure should energetically lower the transition state(s) of the sixth addition step. A similar hexakis-adduct **25** was also formed in 85% yield by *Bingel* addition of **17** to pentakis-adduct **23** (Scheme 6).

Scheme 6. Synthesis of Hexakis-adducts **24** and **25**

a) (EtO₂C)CHBr (10 equiv.), DBU (10 equiv.), PhCl, r.t.; 73%. b) **17** (2 equiv.), DBU (2 equiv.), PhCl, r.t.; 85%.

For the construction of derivatives of the novel fullerene-acetylene hybrid carbon allotropes **26** and **27** described below, a diethynylmethano residue was introduced into the remaining reactive *e*-6-6 bond of pentakis-adduct **21**. First, 3-bromo-1,5-bis(trimethylsilyl)penta-1,4-diyne (5 equiv.; **28**) [40] was reacted with **19** in the presence of DBU (5 equiv.) in PhCl. However, no conversion was observed, and unchanged starting material was recovered, whereas C₆₀ is readily cyclopropanated under these conditions [23]. Tris-adduct **12** also was unreactive under these conditions which again illustrates the significant changes in reactivity of the fullerene that occur with increasing functionalization and reduction of its conjugated π -chromophore. To lower the activation barriers of this polar *Bingel*-type addition reaction, we switched to more polar solvents. Whereas, with **21**, no reaction occurred in CH₂Cl₂, partial conversion was observed in THF, and in Me₂SO, ultimately a clean, rapid conversion to the dialkynyl-methanofullerene **29** [20] was observed (Scheme 7). Thus, reaction of **21** with **28** (10 equiv.) and DBU (10 equiv.) in Me₂SO gave, after chromatography, hexakis-adduct **29** in 88% yield.

The ¹H-NMR spectrum of **29** displayed a single Me₃Si resonance indicating the symmetrical attachment of the dialkynylmethylene group. The 17 resonances for the

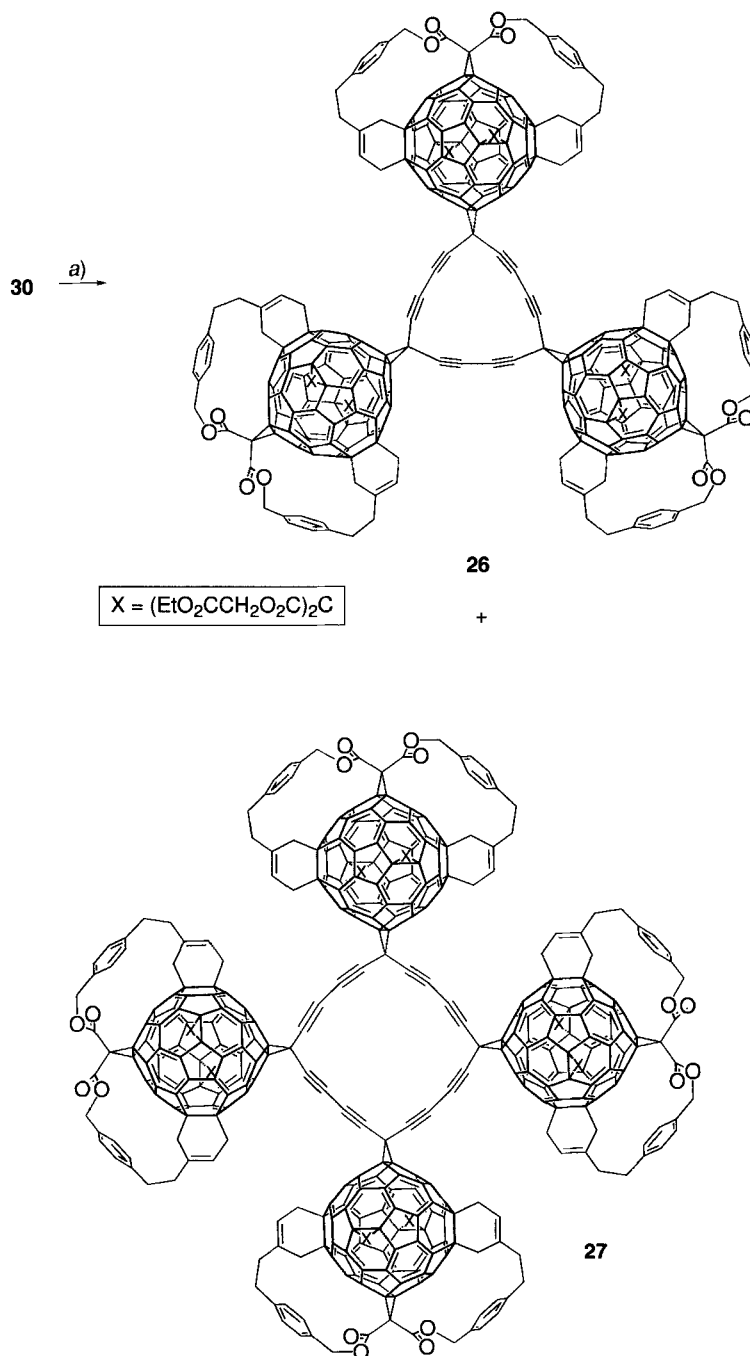
Scheme 7. Synthesis of the Dialkynylmethanofullerenes **29** and **30**

a) DBU (10 equiv.), Me_2SO , r.t.; 88%. b) TBAF (2.75 equiv.) on SiO_2 , dry THF, r.t.; 90%.

fullerene C-atoms in the ^{13}C -NMR spectrum provided conclusive proof for the depicted C_{2v} -symmetrical structure. The MALDI-TOF mass spectrum in α -cyano-4-hydroxycinnamic acid (CCA) as the matrix gave the expected molecular ion at m/z 1918, but the base peak was the fragment at m/z 1711 resulting from loss of the dialkynylmethylene group from the molecule under regeneration of the pentakis-adduct ion $\mathbf{21}^{+}$ [12]. It has in the meanwhile been confirmed by another study [20] that the diethynylmethano group is bound less tightly to the fullerene core than malonate addends and, therefore, splits off first under the MALDI-TOF MS conditions.

Attempts to remove the Me_3Si protecting groups in **29** under basic conditions (K_2CO_3 , MeOH/THF) were unsuccessful and led to products resulting from cleavage of the benzyl ester moieties. In contrast, treatment of **29** with Bu_4NF on SiO_2 in anhydrous THF caused a very clean deprotection affording the diethynyl derivative **30** in 90% yield after chromatography (SiO_2 -H, $\text{CH}_2\text{Cl}_2/\text{AcOEt}$ 100:1.5) [12] [20]. This successful reaction again illustrates the differences in reactivity between lower and higher C_{60} -adducts: when Rubin and coworkers applied Bu_4NF to deprotect 61,61-bis[(trimethylsilyl)ethynyl]-1,2-dihydro-1,2-methano[60]fullerene, mainly decomposition and polymerization of the mono-adduct occurred, presumably induced by attack of the nucleophilic F^- anion [41]. The MALDI-TOF mass spectrum of **30** again showed a pronounced preference for loss of the diethynylmethano over the malonate ester groups.

2.7. Synthesis of Soluble Derivatives of C_{195} and C_{260} . With the C_{2v} -symmetrical hexakis-adduct **30**, an ideal precursor for the oxidative cyclization to acetylenic macrocycles [42] with appended fullerenes had been prepared. Chemical equivalency of the two ethynyl residues in **30** should ensure formation of isomerically pure compounds rather than diastereoisomer mixtures, and the extra functional groups on the fullerene sphere were expected to render the targeted multinanometer-sized products sufficiently soluble for full characterization. Oxidative cyclization of **30** ($c = 0.3$ mM) under Glaser-Hay conditions [42c] [43] (CuCl , N,N,N',N' -tetramethylethylenediamine (TMEDA), air, CH_2Cl_2) failed to produce isolable amounts of the cyclic oligomers. However, when a solution of **30** ($c = 0.16$ mM) was subjected to the Eglinton-Glaser coupling conditions [44], two major products were detected by TLC ($\text{SiO}_2/\text{AcOEt}$ 100:5). Isolation of the two yellow compounds was achieved by chromatography (SiO_2 -H, $\text{CH}_2\text{Cl}_2/\text{AcOEt}$ 100:5

Scheme 8. *Synthesis of Soluble Derivatives 26 and 27 of C₁₉₅ and C₂₆₀, Respectively*

a) $\text{Cu}(\text{OAc})_2$ (200 equiv.), $\text{C}_5\text{H}_5\text{N}$, molecular sieves (4 Å), Ar, 28 h, r.t.; 32% (**26**), 21% (**27**).

then 100:8.5), and their structures were established as cyclic trimeric D_{3h} -symmetrical **26** and cyclic tetrameric D_{4h} -symmetrical **27** based on their spectroscopic properties (Scheme 8). The combined yield of **26** and **27** was a remarkable 53%. Larger cyclic oligomers were not detected in the reaction mixture, perhaps due to steric interaction between the laterally appended fullerene spheres.

The ^1H -NMR spectra of both cyclic oligomers showed no signals for terminal acetylenic protons, two independent sets of CH_2COOEt resonances, and one set of peaks for the tether-cyclohexene moieties. In the ^{13}C -NMR spectra of both **26** and **27**, 17 resonances were visible for the fullerene-core C-atoms implying local C_{2v} symmetry which, when combined with a single peak for the methano C-atom and only two acetylenic C-atom resonances, indicates overall D_{nh} symmetry. The acetylenic C-atom resonances in **26** appeared at 88.41 and 71.77 ppm, whereas those in **27** are located at 75.77 and 69.49 ppm, with the differences in chemical shift presumably reflecting the different bending of the butadiynediyl fragments from linearity in the two compounds. The UV/VIS spectra of **26** and **27** are similar to those of monomeric **30**, with the exception of the increase in molar extinction coefficients as the number of fullerene moieties per molecule increases (Fig. 3). This close spectral resemblance is an indication for the absence of strong homo-conjugation in the acetylenic macrorings as well as for the absence of particular interactions between the laterally appended fullerene chromophores.

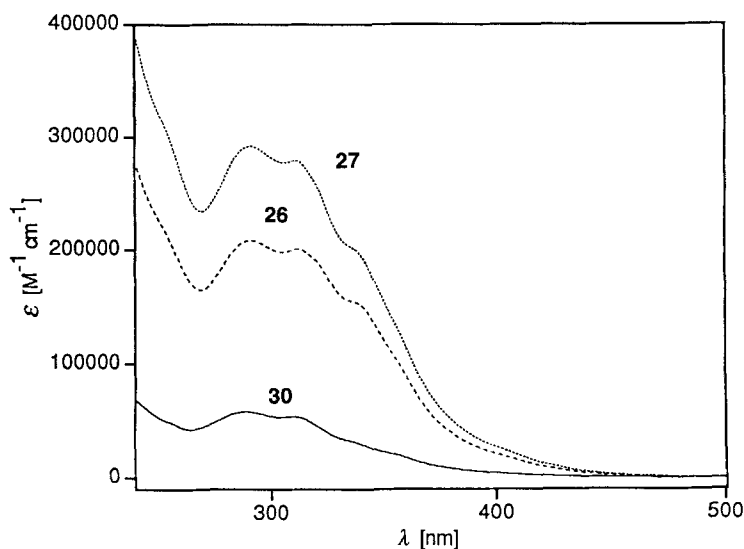


Fig. 3. Electronic absorption spectra recorded for **30** (—), **26** (---), and **27** (·····) in CH_2Cl_2

The size of the cyclic oligomers was determined by MALDI-TOF MS. In the spectrum of **26** (Fig. 4, a), the product with the higher R_f value, the expected molecular ion appeared at m/z 5317 ($\text{C}_{348}\text{H}_{174}\text{O}_{60}$ requires 5314) along with weaker peaks at higher masses which can be ascribed to matrix adducts of the cyclic oligomers. Strong fragment ions confirmed the large propensity of dialkynylmethanofullerenes, as noted above for

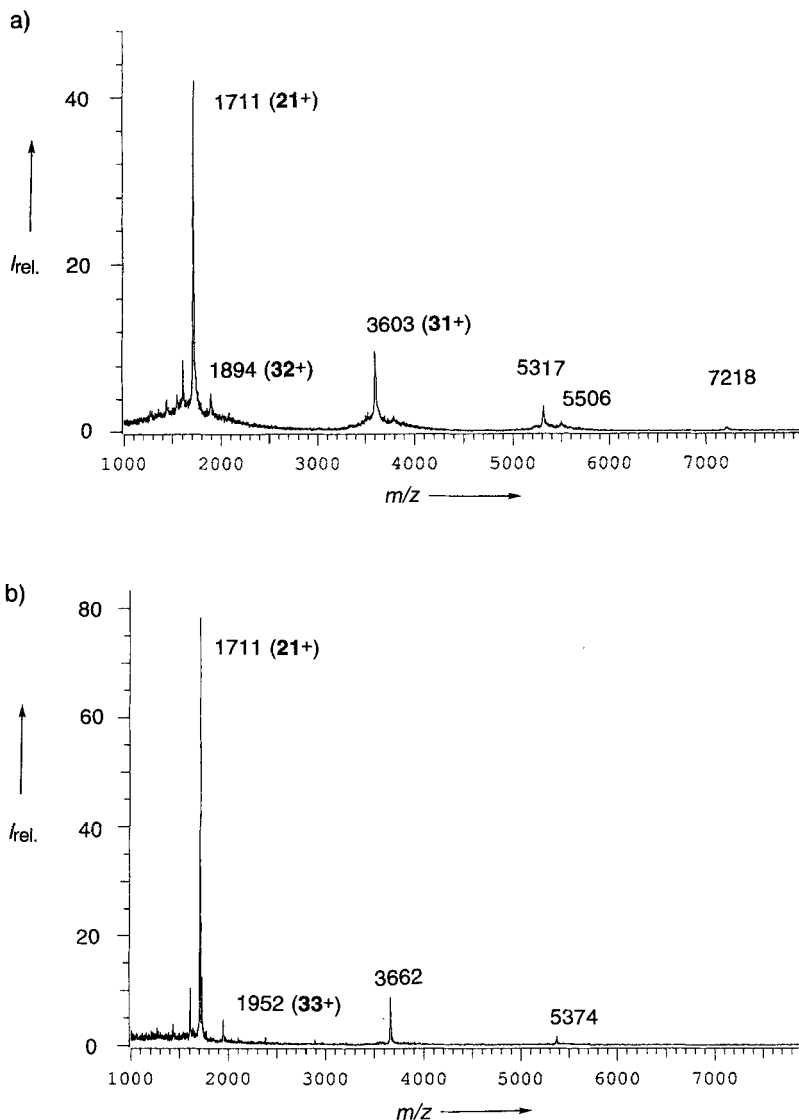
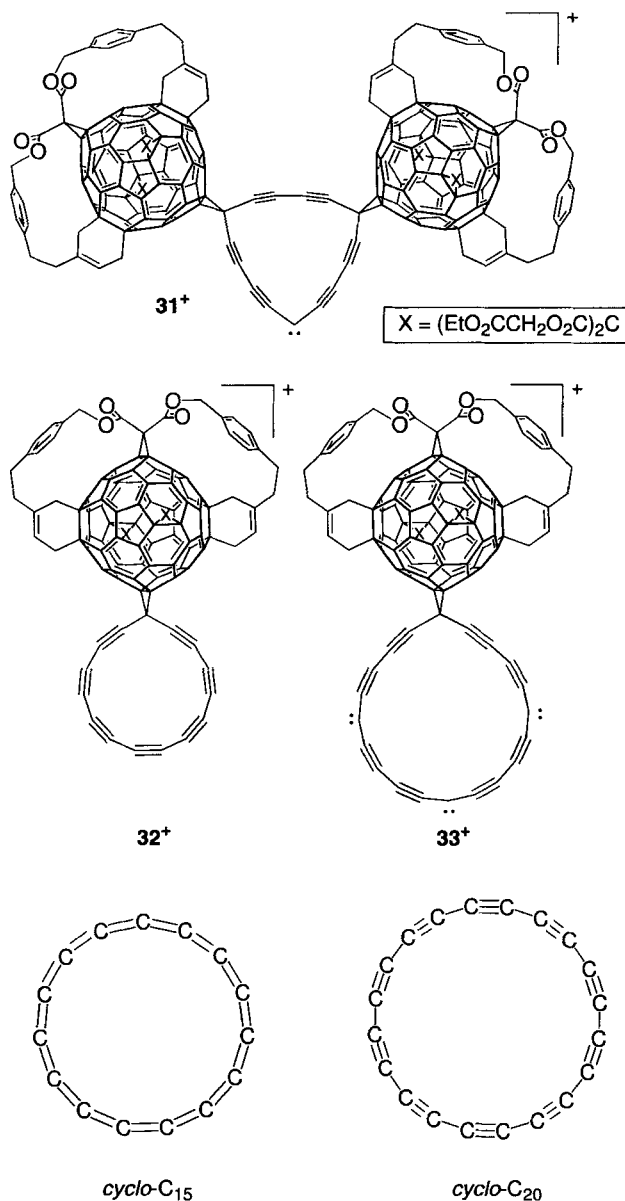


Fig. 4. MALDI-TOF Mass spectra a) of **26** recorded in α -cyano-4-hydroxycinnamic acid (CCA) and b) of **27** in 2,5-dihydroxybenzoic acid (DHB)

29 and **30**, to undergo *retro*-addition with loss of the fullerene moiety. The base peak appeared at m/z 1711, which corresponds to the fullerene pentakis-adduct ion 21^+ . This interesting fragmentation also explains the relatively intense fragment ions at m/z 3603 ($C_{237}H_{116}O_{40}$ requires 3602) and 1894 ($C_{126}H_{58}O_{20}$ requires 1891) which arise from loss of one and two fullerene pentakis-adducts **21**, generating 31^+ and 32^+ . The latter ions correspond to bis- and mono-fullerene adducts of *cyclo*- C_{15} respectively. Unfortunately,



it was not possible to observe a peak for cyclo-C_{15}^+ itself, resulting from *retro*-addition of all three fullerene moieties, since matrix peaks severely obscured the spectrum in the mass region around m/z 180. The corresponding spectrum recorded without matrix assistance also did not yield the cyclocarbon ion peak since, at the required higher laser power, significant fragmentation of the solubilizing groups occurred, once again obscuring the mass region around m/z 180.

The MALDI-TOF mass spectrum of the cyclization product **27** with the lower R_f value did not show a peak at masses expected for tetrameric (m/z 7085), pentameric (m/z 8856), or hexameric (m/z 10628) cyclic oligomers (Fig. 4, b). However, a weak peak was observed at m/z 5374 ($C_{353}H_{174}O_{60}$ requires 5374) and a relatively strong one at m/z 3662 ($C_{242}H_{116}O_{40}$ requires 3662). In analogy to the fragmentation pattern observed for trimeric **26**, these peaks correspond to ions formed by successive loss of one and two molecules of pentakis-adduct **21** from cyclic tetrameric **27**. The weak peak at m/z 1952 ($C_{131}H_{58}O_{20}$ requires 1951) resulted from the loss of a third equivalent of **21** and corresponds to 33^+ , an adduct between fullerene derivative **21** and *cyclo*- C_{20} . These characteristic fragment peaks provide strong support for the assignment of the cyclic tetrameric structure **27** to the product with lower R_f value. Just as in the spectrum of cyclic trimeric **26**, matrix peaks prevented the unambiguous observation of a peak for free *cyclo*- C_{20}^+ . The formation and observation of free *cyclo*- C_{15} and *cyclo*- C_{20} ions, starting from **26** and **27**, respectively, and study of their gas-phase ion-molecule coalescence reactions requires further investigation by Fourier-transform mass spectrometry, a technique which had previously been successfully applied to the study of other cyclocarbon molecules [45–47].

3. Conclusions. – The concept of tether-directed remote functionalization, which had been previously developed by Breslow [10] for the efficient, regioselective functionalization of steroids and long-chain alkanes, is a similarly powerful methodology when applied to the regioselective formation of C_{60} multiple adducts. Some of the specific multiple addition patterns displayed by the compounds in this paper may also be accessed by stepwise functionalization accompanied, however, by tedious chromatographic separations, whereas others can only be obtained by tether-directed synthesis. As an example, the addition pattern in C_{2v} -symmetrical tris-adduct **12**, which is a versatile intermediate in the regioselective synthesis of many other higher adducts of C_{60} and is available in multi-gram quantities through use of the described new methodology, cannot be accessed otherwise.

Starting from **12**, a series of tetrakis- to hexakis-adducts of C_{60} was prepared via the amazing succession of stepwise *e*-additions which had been demonstrated first by Hirsch and coworkers [9e]. In an extension of the regioselectivity concept of preferential *e*-additions, experimental evidence for the enhanced reactivity of e_{face} over e_{edge} bonds was obtained for the first time. The four hexakis-adducts **24**, **25**, **29**, and **30** all possess a pseudo-octahedral addition pattern, and the chromophore of the carbon sphere in these derivatives is reduced to a ‘cubic cyclophane’-type substructure with eight benzenoid rings. X-Ray crystallographic analysis of **24** [39] had shown that bond alteration in these benzenoid rings is significantly reduced as compared to that seen for 6-6 (shorter) and 6-5 bonds (longer) in the parent fullerene and in lower adducts [23].

Oxidative cyclization of diethynylmethanofullerene **30** under Eglinton-Glaser conditions afforded the first soluble derivatives of C_{195} and C_{260} , **26** and **27**, respectively, which are members of a new class of fullerene-acetylene hybrid C-allotropes with the general formula $C_{n(60+5)}$. Particularly intriguing were the MALDI-TOF-MS of **26** and **27** which showed sequential loss of the fullerene spheres generating ions corresponding to mono-fullerene adducts of the cyclocarbons *cyclo*- C_{15} and *cyclo*- C_{20} . This paper once again confirms [48] in an impressive way, that MALDI-TOF-MS is the

premier method for the analysis of the molecular composition of large all-C and C-rich materials.

With increasing functionalization and corresponding reduction of the conjugated fullerene π -chromophore, the reactivity and the physical properties of the carbon spheres change dramatically. In this paper, we briefly discussed the changes in color from magenta-purple (C_{60}) to yellow (hexakis-adducts **24**, **25**, **29**, and **30**) as a consequence of chromophore reduction. Also mentioned were changes in chemical reactivity such as the reduced ability of the hexakis-adducts to act as photosensitizers for 1O_2 formation or the reduced electrophilicity of higher adducts due to the increase in LUMO energy with increasing π -chromophore reduction. A full discussion of the changes in fullerene properties with increasing functionalization is given in the following paper [24], which also reports an important extension of the synthetic methodology presented here. By removal of the tether-reactive-group conjugate, a variety of other multiply functionalized fullerenes with unprecedented addition patterns have become available.

This work was supported by the *Swiss National Science Foundation*. We also thank Ms. *Brigitte Brandenberg* for recording highfield ^{13}C -NMR spectra and Dr. *Walter Amrein* and Mr. *Hans-Ulrich Hediger* for the MALDI-TOF mass spectra.

Experimental Part

General. Reagents and solvents were reagent-grade commercials and were used without further purification. Fullerene soot extract was purchased from *MER Corporation*, Tucson, Arizona, AZ 85706, USA. Crude fullerene-enriched soot, containing 5% soluble fullerenes, was purchased from *Polygon Enterprises*, Waco, Texas, USA, and *Texas Fullerene Corporation*, Houston, Texas, USA. C_{60} was purified as previously reported [49]. THF was freshly distilled from sodium benzophenone ketyl, CH_2Cl_2 from CaH_2 . Me_2SO was distilled from CaH_2 onto activated molecular sieves (4 Å) and stored under N_2 . Anhyd. $PhCl$ was dried over molecular sieves (4 Å) for several days before use. Molecular sieves (4 Å) were activated by heating in a drying pistol to 300° for 6 h and stored in a dessicator over $NaOH$. All reactions were performed in standard glassware under an inert atmosphere (N_2 or Ar). Reactions involving the multiply functionalized fullerenes were conducted under strict exclusion of light and air. Degassing of solvents was performed by repetitive freeze-pump-thaw cycles or by sparging with Ar before use. Evaporation and concentration was done at water-aspirator pressure; if not stated otherwise, isolated solid products were dried at 10^{-1} Torr. Column chromatography (CC) and flash chromatography (FC): SiO_2 -60 (230–400 mesh, 0.040–0.063 mm) from *E. Merck* or *Macherey-Nagel* and SiO_2 -H (0.005–0.040 mm) from *Fluka*. Thin-layer chromatography (TLC): plastic sheets pre-coated with SiO_2 -G UV_{254} from *Macherey-Nagel* and glass-backed SiO_2 -60 F_{254} from *Merck*, visualization by UV light. Melting points: *Büchi Smp-20*; uncorrected. UV/VIS Spectra: *Varian-Cary-5* spectrophotometer; λ_{max} in nm (ϵ). IR Spectra (cm^{-1}): *Perkin-Elmer 1600-FTIR*. NMR Spectra: *Bruker AM 500* (^{13}C) and *Varian Gemini 300* or *200* (1H) at 296 or 300 K, with Me_4Si or solvent peaks ($CHCl_3$ at 7.26 (1H) and 77.0 (^{13}C), C_6HD_5 at 7.15 and 128.0, $CHCl_2CDCl_2$ at 5.91 and 74.2, and CHD_2COCD_3 at 2.04 and 29.8 ppm) as reference. MALDI-TOF Mass spectra (m/z (%)): *Bruker REFLEX* spectrometer with 2,5-dihydroxybenzoic acid (DHB), 2-(4-hydroxyphenylazo)benzoic acid (HABA), or α -cyano-4-hydroxycinnamic acid (CCA) as matrix, positive-ion mode; a 1- μ l sample of the mixture of a soln. of the fullerene derivative (1 μ l; 1 mg ml^{-1}) and a soln. of the matrix (1 μ l) in $MeCN/EtOH/H_2O$ 50:45:5 was deposited on the probe tip, dried under mild vacuum, and analyzed. FAB-MS (m/z , (%)): *VG-ZAB-2-SEQ* instrument; 3-nitrobenzyl alcohol as matrix. For MALDI-TOF and FAB mass spectra of fullerene derivatives, the experimentally observed highest peak in the molecular-ion cluster is reported, followed in parenthesis by the isotopic molecular formula corresponding to the calculated most intense peak in the cluster. Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH-Zürich. Fullerene derivatives were named by the *Chemical Abstracts Service (CAS)* and adjusted for publication.

4-(*Bromomethyl*)benzyl Acetate (**7**). A mixture of **6** (10.0 g, 37.9 mmol), $AcOK$ (3.72 g, 37.9 mmol), $MeCN$ (300 ml), and [18]crown-6 (0.50 g, 1.9 mmol) in $MeCN$ (300 ml) was stirred at r.t. for 16 h. The residue obtained by evaporation was dissolved in Et_2O , washed with 0.1M HCl , H_2O , and sat. aq. $NaCl$ soln., and dried ($MgSO_4$). After concentration, FC (SiO_2 , $PhMe$ /hexane 2:1) gave **7** (4.37 g, 47%) as a colorless oil which solidified on

standing in the freezer overnight. White solid. M.p. ca. 25°. IR (neat): 3031w, 2958w, 2889w, 1740s, 1515w, 1440m, 1421m, 1379m, 1361m, 1229s, 1030m, 968w, 822m. ¹H-NMR (300 MHz, CDCl₃): 7.39 (*d*, *J* = 8.2, 2H); 7.34 (*d*, *J* = 8.2, 2H); 5.10 (*s*, 2H); 4.49 (*s*, 2H); 2.11 (*s*, 3H). ¹³C-NMR (75 MHz, CDCl₃): 170.7; 137.7; 136.2; 129.2; 128.5; 65.7; 32.9; 21.0. EI-MS: 244/242 (0.9, *M*⁺), 202/200 (0.3), 185/183 (1.5), 163 (51), 43 (100, CH₃CO⁺). HR-MS: 241.9946 (*M*⁺, C₁₀H₁₁⁷⁹BrO₂⁺, calc. 241.9943). Anal. calc. for C₁₀H₁₁BrO₂ (243.10): C 49.41, H 4.56, Br 32.87; found: C 49.17, H 4.61, Br 33.01.

4-(3-Methylidenepent-4-enyl)benzyl Acetate (8). Granulated Zn cut into small pieces (3.626 g, 55.47 mmol) was activated by heating with 1,2-dibromoethane (268 mg, 1.43 mmol) in THF (5 ml) near reflux for 2 min. After decanting the solvent, **7** (8.66 g, 35.6 mmol) in THF (30 ml) was added over 75 min by syringe pump to the activated Zn cooled to 5°. After 3 h at 5°, the soln. was transferred by syringe into a soln. of CuCN (*caution!*) (3.19 g, 35.6 mmol) and LiCl (3.10 g, 73.0 mmol) in THF (45 ml) at –75°. The resultant mixture was brought to –20° for 5 min and then cooled to below –70°. After 2-(bromomethyl)buta-1,3-diene (4.19 g, 28.5 mmol) was added by syringe, the mixture was allowed to warm to r.t. over 14 h, then quenched with 25% aq. NH₄OH/sat. aq. NH₄Cl soln. 1:1, diluted with Et₂O, and washed with 25% aq. NH₄OH/sat. aq. NH₄Cl soln. 1:1 until the washings were colorless. After washing with 0.1M HCl, sat. aq. NaHCO₃ soln., H₂O, and sat. aq. NaCl soln., the org. phase was dried (MgSO₄) and evaporated. CC (SiO₂, PhMe) gave **8** (3.99 g, 61%). Colorless oil. IR (neat): 3089w, 3011w, 2936w, 2861w, 1741s, 1594w, 1515w, 1379m, 1361m, 1229s, 1020m, 899m, 811w. ¹H-NMR (200 MHz, CDCl₃): 7.30 (*d*, *J* = 8.3, 2H); 7.21 (*d*, *J* = 8.3, 2H); 6.41 (*dd*, *J* = 17.8, 10.8, 1H); 5.35–4.95 (*m*, 4H); 5.08 (*s*, 2H); 2.90–2.75 (*m*, 2H); 2.60–2.45 (*m*, 2H); 2.10 (*s*, 3H). ¹³C-NMR (50 MHz, CDCl₃): 170.9; 145.4; 142.3; 138.7; 133.9; 128.5; 128.4; 116.1; 113.2; 66.1; 34.1; 33.1; 21.0. EI-MS: 230 (0.5, *M*⁺), 170 (100, [M – C₂H₄O₂]⁺). HR-MS: 230.1340 (*M*⁺, C₁₅H₁₈O₂⁺, calc. 230.1307).

4-(3-Methylidenepent-4-enyl)benzenemethanol (2). A mixture of **8** (1.240 g, 5.38 mmol) and K₂CO₃ (3.720 g, 26.92 mmol) in MeOH (50 ml) was stirred at r.t. for 1 h. Dilution with Et₂O, washing with 0.1M HCl, H₂O, sat. aq. NaCl soln., drying (MgSO₄), and CC (SiO₂, CH₂Cl₂) gave **2** (0.975 g, 96%). Colorless oil. IR (neat): 3339s, 3083m, 2927s, 2861m, 1593s, 1513m, 1419m, 1215w, 1038m, 1014s, 992s, 897s, 803m, 756w. ¹H-NMR (200 MHz, CDCl₃): 7.30 (*d*, *J* = 8.0, 2H); 7.21 (*d*, *J* = 8.0, 2H); 6.41 (*dd*, *J* = 17.7, 10.8, 1H); 5.35–4.95 (*m*, 4H); 4.66 (*s*, 2H); 2.90–2.75 (*m*, 2H); 2.60–2.45 (*m*, 2H); 1.90–1.60 (*br. s*, 1H). ¹³C-NMR (50 MHz, CDCl₃): 145.5; 141.7; 138.7; 138.4; 128.6; 127.1; 116.1; 113.3; 65.2; 34.2; 33.3. EI-MS: 188 (9, *M*⁺), 170 (8), 158 (40), 129 (47), 121 (100, C₈H₉O⁺), 91 (40), 77 (30). HR-MS: 188.1217 (*M*⁺, C₁₃H₁₆O⁺, calc. 188.1201). Anal. calc. for C₁₃H₁₆O (188.27): C 82.94, H 8.57; found: C 82.67, H 8.47.

[4-(3-Methylidenepent-4-enyl)phenyl]methyl 3'H-Cyclopropa[1,9][5,6]fullerene-C₆₀-I_n-3'-carboxylate (3) and 3',6'-Dihydro-5',3'-(Ethano[1,4]benzenomethanoxymethano)-3'H-benzo[1,9]cyclopropa[16,17][5,6]fullerene-C₆₀-I_n-17-one (4). To **1** (100 mg, 0.128 mmol) in PhBr (20 ml) was added sequentially DCC (26.5 mg, 0.128 mmol), HOBt (17.4 mg, 0.128 mmol), DMAP (15.7 mg, 0.128 mmol), and **2** (48.4 mg, 0.256 mmol). After stirring at r.t. for 19 h, the mixture was loaded directly onto a column and chromatographed (SiO₂, PhMe/hexane 2:1), yielding a soln. of **3** which was evaporated to remove the hexane and then diluted with PhMe to a total volume of 500 ml. The resulting soln. was deoxygenated by purging with Ar for 10 min, further degassed by two freeze-pump-thaw cycles, and then heated to 80° for 44 h. After concentration to 100 ml, the orange-red soln. was chromatographed (SiO₂, PhMe/hexane 2:1) to afford one main product which was recrystallized from CS₂/MeOH, then from CS₂/hexane, and dried to give **4** (27.7 mg, 23%).

3: Wine-red soln. UV/VIS (PhMe): 692, 495, 429, 331.

4: Black solid. M.p. > 270°. TLC (PhMe/hexane 2:1) *R*_f 0.51. UV/VIS (CH₂Cl₂): 508 (sh, 2180), 449 (3050), 427 (4030), 399 (4000, sh), 397 (3250, sh), 349 (15300, sh), 309 (32000, sh), 279 (51400, sh), 248 (77100). IR (KBr): 2919w, 1740m, 1725m, 1638s, 1617s, 1511s, 1383m, 1181m, 1156m, 525m. ¹H-NMR (300 MHz, CS₂/(CD₃)₂CO capillary): 7.06 (*s*, 4H); 6.47 (*t*, *J* = 5.4, 1H); 5.09 (*s*, 2H); 4.47 (*s*, 1H); 3.66 (*d*, *J* = 5.4, 2H); 3.33 (*s*, 2H); 3.06 (*s*, 4H). ¹³C-NMR (125 MHz, CS₂/(CD₃)₂CO capillary): 163.46; 160.19; 156.41; 149.16; 148.35; 147.90; 147.42; 146.81; 146.53; 146.32; 146.29; 146.26; 145.99; 145.86; 145.33; 145.20; 145.09; 144.99; 144.69; 144.23; 144.11; 144.01; 143.20; 143.14; 142.59; 142.49; 142.22; 140.32; 139.09; 138.97; 138.60; 136.59; 132.72; 130.79; 128.51 (*br.*); 125.98; 69.60; 68.00; 65.78; 64.99; 43.77; 41.71; 40.14; 35.67; 34.75. MALDI-TOF-MS (DHB): 964 (49, [M + O]⁺, ¹²C₇₅H₁₆O₃⁺; formed during sample preparation for MS), 948 (100, *M*⁺, ¹²C₇₅H₁₆O₂⁺). Anal. calc. for C₇₅H₁₆O₂ · 0.8 CS₂ (1009.87): C 90.15, H 1.60; found: C 89.90, H 1.76.

Methyl 4-(3-Methylidenepent-4-enyl)benzyl Propanedioate (11). To a soln. of **2** (1.00 g, 5.31 mmol) in CH₂Cl₂ (20 ml) at –5°, methyl 3-chloro-3-oxopropanoate (725 mg, 0.57 ml, 5.31 mmol) and C₅H₅N (420 mg, 0.43 ml, 5.31 mmol) were added by syringe. After 1.25 h, the mixture was poured into Et₂O, washed with sat. aq. NaHCO₃ soln., 0.1M HCl, H₂O, and sat. aq. NaCl soln. After evaporation, FC (SiO₂, CH₂Cl₂) afforded **11** (1.233 g, 81%). Colorless oil. TLC (CH₂Cl₂/hexane 1:1) *R*_f 0.28. IR (neat): 3089w, 3007w, 2951m, 2863w, 1757s, 1736s, 1594m,

1517m, 1438m, 1410m, 1377m, 1335s, 1274s, 1200m, 1149s, 1019m, 992m, 901m, 813m. $^1\text{H-NMR}$ (200 MHz, CDCl_3): 7.35–7.15 (*AA'BB'*, 4H); 6.41 (*dd*, $J = 10.8$, 17.4, 1H); 5.27 (*d*, $J = 17.4$, 1H); 5.18 (*s*, 2H); 5.10 (*d*, $J = 10.8$, 1H); 5.04 (*br. s*, 1H); 5.00 (*br. s*, 1H); 3.74 (*s*, 3H); 3.43 (*s*, 2H); 2.90–2.75 (*m*, 2H); 2.60–2.45 (*m*, 2H). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3): 166.9; 166.4; 145.5; 142.6; 138.7; 132.8; 128.6; 128.5; 116.1; 113.3; 67.1; 52.3; 41.2; 34.0; 33.0. EI-MS: 288 (0.2, M^+), 221 (12), 170 (100, $\text{C}_{13}\text{H}_{14}^+$). Anal. calc. for $\text{C}_{17}\text{H}_{20}\text{O}_4$ (288.34): C 70.81, H 6.99; found: C 71.03, H 6.85.

Methyl 4-(3-Methylidenepent-4-enyl)benzyl 2-Bromopropanedioate (10). To a soln. of **11** (1.10 g, 3.81 mmol) in THF (20 ml), DBU (696 mg, 4.47 mmol) was added by syringe. After 5 min, the mixture was cooled to -78° and, after 5 min at -78° , a soln. of CBr_4 (1.516 g, 4.57 mmol) in THF (5 ml) was added by syringe. The yellow mixture was quenched after 20 min with 0.1M HCl, diluted with Et_2O , washed with 0.1M HCl, sat. aq. NaHCO_3 , and sat. aq. NaCl soln., and dried (MgSO_4). After evaporation, CC (SiO_2 , CH_2Cl_2 /hexane 1:1) provided **10** (955 mg, 68%). Colorless oil. TLC (CH_2Cl_2 /hexane 1:1): R_f 0.40. IR (neat): 3088w, 3006w, 2954w, 2861w, 1767s, 1747s, 1594m, 1516w, 1436m, 1376w, 1308m, 1288m, 1144s, 1015m, 994m, 900m, 816w, 651w. $^1\text{H-NMR}$ (200 MHz, CDCl_3): 7.35–7.20 (*AA'BB'*, 4H); 6.41 (*dd*, $J = 10.8$, 17.5, 1H); 5.28 (*d*, $J = 17.5$, 1H); 5.23 (*s*, 2H); 5.10 (*d*, $J = 10.8$, 1H); 5.05 (*br. s*, 1H); 5.00 (*br. s*, 1H); 4.89 (*s*, 1H); 3.81 (*s*, 3H); 3.90–3.75 (*m*, 2H); 2.60–2.45 (*m*, 2H). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3): 164.9; 164.3; 145.3; 142.8; 138.6; 132.0; 128.6; 128.4; 116.1; 113.3; 68.6; 53.8; 41.9; 34.1; 33.1. EI-MS: 368/366 (1, M^+), 170 (100, $\text{C}_{13}\text{H}_{14}^+$). Anal. calc. for $\text{C}_{17}\text{H}_{19}\text{BrO}_4$ (367.24): C 55.60, H 5.21, Br 21.76; found: C 55.86, H 5.22, Br 21.66.

Methyl 3',6-Dihydro-17'-oxo-5',3''-(ethano[1,4]benzenomethanoxy-methano)-3"-H-benzo[1,9]cyclopropa-[16,17][5,6]fullerene- C_{60} -I $_h$ -3"-carboxylate (9). To a soln. of C_{60} (735 mg, 1.02 mmol) and **10** (250 mg, 0.68 mmol) in PhMe (500 ml), DBU (104 mg, 0.680 mmol) in PhMe (3 ml) was added by syringe. After 1 h, the mixture was concentrated to 200 ml, diluted with hexane (200 ml), and submitted to CC (SiO_2 , PhMe/hexane 1:1 then 2:1): wine-red soln. of the methanofullerene mono-adduct. After evaporation of hexane, the remaining soln. was diluted with PhMe (to 1 l), deoxygenated by bubbling Ar through for 10 min, and heated to reflux for 39 h. Concentration to 100 ml and CC (SiO_2 , PhMe), followed by recrystallization from CS_2 /MeOH, yielded **9** (340 mg, 50%). Brown solid. M.p. $> 250^\circ$. TLC (PhMe): R_f 0.70. UV/VIS (CH_2Cl_2): 500 (sh, 2120), 450 (2940), 428 (3830), 399 (sh, 3560), 338 (sh, 21100), 305 (sh, 39500), 271 (sh, 61100), 249 (85700). IR (KBr): 2944w, 2914w, 2831w, 1747s, 1725s, 1513w, 1446m, 1431m, 1321m, 1288m, 1097m, 1061m, 585w, 533m, 524m. $^1\text{H-NMR}$ (200 MHz, $\text{CS}_2/\text{CDCl}_3$ 1:1): 7.30–7.05 (*br. m*, 4H); 6.55 (*t*, $J = 5.5$, 1H); 5.30–5.10 (*br. s*, 2H); 4.01 (*s*, 3H); 3.72 (*d*, $J = 5.5$, 2H); 3.48 (*br. s*, 2H); 3.11 (*br. s*, 4H). $^{13}\text{C-NMR}$ (125 MHz, $\text{CS}_2/\text{C}_2\text{D}_2\text{Cl}_4$ 1:1): 163.99; 162.11; 160.62; 156.28 (*br.*); 149.19; 148.36; 148.01; 147.35; 147.01; 146.40 (*br.*); 146.23; 146.22; 145.81; 145.74; 144.96; 144.90; 144.84; 144.55; 144.25; 144.10; 144.06; 143.28; 142.80; 142.68 (*br.*); 142.55; 142.53; 141.58; 141.72; 139.70 (*br.*); 138.85; 138.43 (*br.*); 132.08; 130.32; 128.46 (*br.*); 126.03; 69.95; 68.55; 65.22; 64.92; 53.78; 52.42; 43.84; 40.03; 35.89; 33.92. FAB-MS: 1007 (44, MH^+ , $^{13}\text{C}^{12}\text{C}_{76}\text{H}_{18}\text{O}_4^+$), 720 (100, C_{60}^+). Anal. calc. for $\text{C}_{77}\text{H}_{18}\text{O}_4 \cdot 0.15 \text{CS}_2$ (1018.41): C 90.99, H 1.78; found: C 90.87, H 1.84.

Bis[4-(3-methylidenepent-4-enyl)benzyl] Propanedioate (14). To a soln. of **2** (829 mg, 4.40 mmol) and propanedioyl dichloride (310 mg, 2.20 mmol) in CH_2Cl_2 (20 ml) at 0° , $\text{C}_5\text{H}_5\text{N}$ (348 mg, 0.36 ml, 4.40 mmol) was added by syringe. After stirring for 3 h, the mixture was diluted with Et_2O , the soln. washed with sat. aq. NaHCO_3 soln., 0.1M HCl, H_2O , sat. aq. NaCl soln., dried (MgSO_4), and evaporated, and the residue chromatographed (SiO_2 , CH_2Cl_2): **14** (780 mg, 80%). Colorless oil. IR (neat): 3087w, 2936w, 2862w, 1753s, 1736s, 1594m, 1515m, 1459w, 1410w, 1377m, 1330m, 1269m, 1146m, 992m, 900m, 812m. $^1\text{H-NMR}$ (200 MHz, CDCl_3): 7.27 (*d*, $J = 8.2$, 4H); 7.19 (*d*, $J = 8.2$, 4H); 6.40 (*dd*, $J = 17.6$, 10.8, 2H); 5.35–4.95 (*m*, 8H); 5.14 (*s*, 4H); 3.46 (*s*, 2H); 2.90–2.75 (*m*, 4H); 2.60–2.45 (*m*, 4H). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3): 166.4; 145.5; 142.6; 138.8; 132.8; 128.6; 128.5; 116.2; 113.3; 67.1; 41.5; 34.1; 33.1. EI-MS: 444 (2, M^+), 104 (100, C_8H_8^+). HR-MS: 444.2290 (M^+ , $\text{C}_{29}\text{H}_{32}\text{O}_4^+$, calc. 444.2300). Anal. calc. for $\text{C}_{29}\text{H}_{32}\text{O}_4$ (444.58): C 78.35, H 7.26; found: C 78.45, H 7.31.

Bis[4-(3-methylidenepent-4-enyl)benzyl] 2-Bromopropanedioate (13). To a soln. of **14** (472 mg, 1.06 mmol) in THF (20 ml) at r.t., DBU (194 mg, 1.27 mmol) in THF (3 ml) was added. After 5 min, the mixture was cooled to -78° , and CBr_4 (423 mg, 1.27 mmol) in THF (5 ml) was added. Within 75 min, the soln. was warmed to -65° and quenched with 0.1M HCl, diluted with Et_2O , washed with 0.1M HCl, H_2O , sat. aq. NaCl soln., dried (MgSO_4) and evaporated. CC (SiO_2 , hexane/ CH_2Cl_2 1:1) afforded **13** (441 mg, 79%). Colorless oil. IR (neat): 3087w, 2939w, 1763s, 1744s, 1594m, 1515w, 1458w, 1421w, 1374w, 1281m, 1231m, 1142m, 992m, 899m, 814m. $^1\text{H-NMR}$ (200 MHz, CDCl_3): 7.25 (*d*, $J = 8.4$, 4H); 7.18 (*d*, $J = 8.4$, 4H); 6.40 (*dd*, $J = 17.4$, 10.8, 2H); 5.35–4.95 (*m*, 8H); 5.19 (*s*, 4H); 4.90 (*s*, 1H); 2.90–2.75 (*m*, 4H); 2.60–2.45 (*m*, 4H). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3): 164.1; 145.3; 142.6; 138.6; 132.0; 128.5; 128.4; 116.1; 113.2; 68.5; 42.3; 34.1; 33.0. EI-MS: 524/522 (1, M^+), 171 (91), 104 (100, C_8H_8^+). Anal. calc. for $\text{C}_{29}\text{H}_{31}\text{BrO}_4$ (523.47): C 66.54, H 5.97, Br 15.26; found: C 66.66, H 6.11, Br 15.21.

Bis[4-(3-methylenepent-4-enyl)phenyl]methyl 3'-H-Cyclopropa[1,9][5,6]fullerene-C₆₀-I_h-3',3'-dicarboxylate (15) and 3',3',6',6'-Tetrahydro-5',3''':5'',3'''-bis(ethano[1,4]benzenomethanoxymethano)-3'''H-dibenzo[1,9:52,60]-cyclopropa[16,17][5,6]fullerene-C₆₀-I_h-17',17''-dione (12). To a soln. of C₆₀ (2.753 g, 3.82 mmol) and **13** (1.0 g, 1.91 mmol) in PhMe (700 ml), DBU (320 mg, 2.10 mmol) in PhMe (50 ml) was added over 5 min. After 3 h, the mixture was concentrated to 100 ml, diluted with hexane (100 ml), and chromatographed (SiO₂, PhMe/hexane 1:1, then 2:1): wine-red methanofullerene **15**. After evaporation of hexane, PhMe was added to give a total volume of 2.5 l, then the soln. was deoxygenated by purging with Ar for 1.5 h and heated to reflux for 36 h. Concentration and CC (SiO₂, PhMe), followed by recrystallization from CHCl₃/MeOH and drying gave **12** (1.335 g, 60%).

15: Wine-red soln. UV/VIS (PhMe): 691, 489, 429, 330. ¹H-NMR (300 MHz, Cl₂CDCDCl₂): aromatic resonances obscured; 6.62 (*dd*, *J* = 11.0, 17.8, 2H); 5.63 (*s*, 4H); 5.48 (*d*, *J* = 17.8, 2H); 5.31 (*d*, *J* = 11.0, 2H); 5.26 (*s*, 2H); 5.21 (*s*, 2H); 3.05–2.95 (*m*, 4H); 2.75–2.65 (*m*, 4H). **12**: Brown solid. M.p. > 270°. TLC (PhMe) *R_f* 0.60. UV/VIS (CH₂Cl₂): 498 (3120), 468 (1660), 368 (sh, 6320), 337 (sh, 13800), 308 (sh, 21000), 264 (41400). IR (KBr): 2919w, 1746m, 1718m, 1638s, 1617s, 1384w, 1288w, 1256w, 1229m, 1208m, 1168w, 1098w, 1061m, 1001w, 946w, 885w, 799m, 744m, 625m, 537m, 525m. ¹H-NMR (300 MHz, Cl₂CDCDCl₂): 7.13 (*br. s*, 8H); 6.52 (*t*, *J* = 5.3, 2H); 5.18 (*s*, 4H); 3.80 (*d*, *J* = 5.3, 4H); 3.42 (*s*, 4H); 3.06 (*s*, 8H). ¹³C-NMR (125 MHz, Cl₂DCCDCl₂): 162.88; 158.36; 153.58; 146.97; 146.50; 146.24; 145.70; 145.51; 145.19; 144.60; 143.09; 142.81; 142.27 (*br.*); 140.17; 139.90; 139.72; 139.57; 132.02; 130.61; 128.62 (*br.*); 125.93; 69.34; 69.13; 62.89; 62.85; 54.45; 43.53; 39.93; 35.49; 34.49. MALDI-TOF-MS (DHB): 1178 (23, [*M* + O]⁺, ¹²C₈₉H₃₀O₅⁺, formed during sample preparation for MS), 1162 (100, *M*⁺, ¹²C₈₉H₃₀O₄⁺). Anal. calc. for C₈₉H₃₀O₄ · 0.75 CHCl₃ (1252.76): C 86.05, H 2.47; found: C 85.94, H 2.74.

Bis(2-ethoxy-2-oxoethyl) Propanedioate (18). To a soln. of propanedioyl dichloride (1.35 g, 9.60 mmol) in CH₂Cl₂ (50 ml) at 0°, ethyl hydroxyacetate (2.00 g, 19.2 mmol) and C₅H₅N (1.52 g, 19.2 mmol) were added over 15 min by syringe. After 75 min at 0°, the ice bath was removed, and stirring was continued at r.t. for 14 h. The mixture was diluted with Et₂O, washed with sat. aq. NaHCO₃ soln., 0.1M HCl, H₂O, sat. aq. NaCl soln., dried (MgSO₄), and evaporated after which bulb-to-bulb distillation (140°/0.2 Torr) provided **18** (1.95 g, 73%). Pale-yellow oil. IR (neat): 2986m, 1748s, 1425s, 1383s, 1292s, 1211s, 1144s, 1071s, 1028s, 943w, 854m, 790w, 731w. ¹H-NMR (200 MHz, CDCl₃): 4.62 (*s*, 4H); 4.18 (*q*, *J* = 7.2, 4H); 3.57 (*s*, 2H); 1.23 (*t*, *J* = 7.2, 6H). ¹³C-NMR (50 MHz, CDCl₃): 166.9; 165.2; 61.4; 61.3; 40.3; 13.9. EI-MS: 277 (0.5, *MH*⁺), 105 (100, C₄H₉O₃⁺). Anal. calc. for C₁₁H₁₆O₈ (276.24): C 47.83, H 5.84; found: C 47.79, H 5.82.

Bis(2-ethoxy-2-oxoethyl) 2-Bromopropanedioate (17). To a soln. of **18** (2.25 g, 8.14 mmol) in THF (20 ml), DBU (1.49 g, 9.77 mmol) was added. After 5 min at r.t., the mixture was cooled to –70°, and a soln. of CBr₄ (3.24 g, 9.77 mmol) in THF (5 ml) was added rapidly by syringe. The resulting suspension was allowed to warm to r.t. overnight. Dilution with Et₂O, washing with H₂O, sat. aq. NaCl soln., drying (MgSO₄), and bulb-to-bulb distillation (140°/0.05 Torr) gave **17** (6.12 g, 75%) contaminated by 3% each of starting material and dibrominated product (¹H-NMR). Further purification by distillation or CC was not possible, but the minor impurities did not affect the subsequent *Bingel* addition and were readily removed afterwards. Pale-yellow oil. IR (neat): 2985m, 1753s, 1424m, 1381s, 1301s, 1208s, 1146s, 1063m, 1030m, 943w, 858w. ¹H-NMR (200 MHz, CDCl₃): 5.07 (*s*, 1H); 4.78 (*d*, *J* = 15.7, 2H); 4.69 (*d*, *J* = 15.7, 2H); 4.24 (*q*, *J* = 7.2, 4H); 1.29 (*t*, *J* = 7.2, 6H). ¹³C-NMR (50 MHz, CDCl₃): 166.3; 163.6; 62.4; 61.7; 40.7; 14.0. EI-MS: 356/354 (1, *M*⁺), 253/251 (50), 207/205 (49), 173 (100, C₇H₉O₃⁺), 105 (99), 69 (59). HR-MS: 353.9933 (*M*⁺, C₁₁H₁₅⁷⁹BrO₈⁺, calc. 353.9951).

Diethyl 3',3',6',6'-Tetrahydro-17',17''-dioxo-5',3''':5'',3'''-Bis(ethano[1,4]benzenomethanoxymethano)-3'''H, 3'''H-dibenzo[1,9:52,60]dicyclopropa[16,17:21,40][5,6]fullerene-C₆₀-I_h-3''':3''':3''':3'''-dicarboxylate (16). To a suspension of **12** (25.0 mg, 0.0215 mmol) and diethyl 2-bromopropanedioate (25.7 mg, 0.107 mmol) in dry PhCl (19.5 ml), DBU (16.4 mg, 0.107 mmol) in PhCl (0.5 ml) was added. After 135 min, the mixture was directly chromatographed (SiO₂, PhMe then CH₂Cl₂) to give a bright-red soln. of **16**. Concentration and precipitation by addition of MeOH, followed by drying yielded **16** (20.4 mg, 72%). Red solid. M.p. > 270°. TLC (PhMe): *R_f* 0.13. UV/VIS (CH₂Cl₂): 578 (1040), 556 (sh, 1350), 533 (sh, 2370), 492 (3550), 459 (3680), 414 (sh, 5620), 386 (8740), 278 (71700). IR (CHCl₃): 3053w, 1740m, 1719m, 1264s, 1015m, 908w, 704m. ¹H-NMR (CDCl₃, 300 MHz): 7.20 (*br. s*, 4H); 7.12 (*br. s*, 4H); 6.41 (*t*, *J* = 5.3, 2H); 5.19 (*s*, 4H); 4.40–4.20 (*m*, 4H); 3.60 (*dd*, *J* = 5.3, 14.1, 2H); 3.56 (*dd*, *J* = 5.3, 14.1, 2H); 3.28 (*d*, *J* = 14.3, 2H); 3.18 (*d*, *J* = 14.3, 2H); 3.06 (*br. s*, 8H); 1.32 (*t*, *J* = 7.1, 3H); 1.30 (*t*, *J* = 7.1, 3H). ¹³C-NMR (CDCl₃, 75 MHz): 163.43; 163.19; 162.42; 158.10; 156.70; 153.27; 152.16; 150.21; 148.14; 147.23; 147.14; 146.19; 146.11; 145.82; 145.35; 145.31; 145.08; 145.00; 144.45 (2 ×); 142.65; 142.44 (2 ×); 141.95; 141.93; 141.85; 141.16; 140.78; 139.82; 139.51; 139.47; 131.85; 130.37; 130.28; 128.25; 125.39; 71.82; 68.61; 67.49; 67.28; 62.74; 62.63; 62.47; 62.25; 53.60; 52.72; 42.82; 39.32; 35.02; 34.23; 14.13 (2 ×). MALDI-TOF-MS (HABA): 1352 (31, [*M* + 2 O]⁺, ¹²C₉₆H₄₀O₁₀⁺), 1336 (31, [*M* + O]⁺, ¹²C₉₆H₄₀O₉⁺) (both peaks due to oxidation during sample preparation for MS), 1320 (100, *M*⁺, ¹²C₉₆H₄₀O₈⁺).

Bis(2-ethoxy-2-oxoethyl) 3',3'',6',6''-Tetrahydro-17',17''-dioxo-5',3''':5'',3''''-Bis(ethano[1,4]benzenomethanoxymethano)-3'''H, 3''''H-dibenzo[1,9:52,60]dicyclopropa[16,17:21,40][5,6]fullerene-C₆₀-I_h-3''''',3''''-dicarboxylate (19). To a suspension of **12** (200 mg, 0.172 mmol) in PhCl (100 ml), **17** (458 mg, 1.29 mmol) and DBU (196 mg, 1.29 mmol) in PhCl (1 ml) were added. The soln. was stirred at r.t. for 125 min, then chromatographed (SiO₂, PhMe then CHCl₃/EtOH 99:1) to separate unreacted starting material from higher adducts. A second CC (SiO₂-H, CH₂Cl₂) gave traces of three isomeric tetrakis-adducts followed by bright-red **19**, along with higher adducts. Recrystallization from CH₂Cl₂/MeOH and drying afforded **19** (173 mg, 70%). Red solid. M.p. 230° (dec.). TLC (CH₂Cl₂): R_f 0.48. UV/VIS (CH₂Cl₂): 578 (750), 493 (2790), 459 (3090), 414 (sh, 4370), 385 (6900), 278 (53400), 241 (sh, 63100). IR (KBr): 2919w, 1751 s, 1636w, 1617w, 1449w, 1383m, 1288m, 1257m, 1233m, 1193s, 1106m, 1061w, 801w, 667m, 536w, 528w. ¹H-NMR (200 MHz, CDCl₃): 7.19 (s, 4H); 7.13 (s, 4H); 6.40 (t, J = 5.4, 2H); 5.18 (br. m, 4H); 4.76 (s, 2H); 4.73 (s, 2H); 4.22 (q, J = 7.1, 2H); 4.19 (q, J = 7.1, 2H); 3.64 (dd, J = 5.4, 14.4, 2H); 3.55 (dd, J = 5.4, 14.4, 2H); 3.28 (d, J = 14.2, 2H); 3.18 (d, J = 14.2, 2H); 3.05 (br. s, 8H); 1.35–1.15 (m, 6H). ¹³C-NMR (75 MHz, CDCl₃): 166.51; 166.36; 162.39; 162.31; 162.17; 158.05; 156.67; 153.24; 152.11; 150.20; 148.09; 147.32; 147.10; 146.17; 146.06; 145.96; 145.78; 145.45; 145.29; 145.10; 144.93; 144.54; 144.45; 142.66; 142.52; 142.38; 141.91; 141.32; 141.12; 140.71; 139.74; 139.59; 139.43; 131.74; 130.29; 128.39 (br.); 128.15 (br.); 125.34; 70.97; 68.58; 67.43; 67.16; 62.41; 62.31; 62.18; 61.60; 61.55; 53.56; 51.33; 42.79; 39.23; 34.98; 34.13; 33.94; 14.10; 14.04. MALDI-TOF-MS (DHB): 1459 (42, [M + Na]⁺, ¹²C₁₀₀H₄₄O₁₂Na⁺), 1437 (100, M⁺, ¹³C¹²C₉₉H₄₄O₁₂⁺), 1335 (13), 1165 (22). Anal. calc. for C₁₀₀H₄₄O₁₂ (1437.44): C 83.56, H 3.09; found: C 82.35, H 3.38.

Tetraethyl 3',3'',6',6''-Tetrahydro-17',17''-dioxo-5',3''':5'',3''''-bis(ethano[1,4]benzenomethanoxymethano)-3'''H, 3''''H,3''''H,3''''H-dibenzo[1,9:52,60]tricyclopropa[16,17:21,40:30,31][5,6]fullerene-C₆₀-I_h-3''''',3''''',3''''',3''''-tetracarboxylate (20) and Tetraethyl 3',3'',6',6''-Tetrahydro-17',17''-dioxo-5',3''':5'',3''''-bis(ethano[1,4]benzenomethanoxymethano)-3'''H,3''''H,3''''H,3''''H-dibenzo[1,9:52,60]tricyclopropa[16,17:21,40:44,45][5,6]fullerene-C₆₀-I_h-3''''',3''''',3''''',3''''-tetracarboxylate (22). To a soln. of **16** (764 mg, 0.578 mmol) in PhCl (50 ml) was added at 0° DBU (660 mg, 4.337 mmol) and diethyl 2-bromopropanedioate (1.04 g, 4.34 mmol). The resulting mixture was stirred for 90 min, then washed with sat. aq. NH₄Cl and sat. aq. NaCl soln., and dried (MgSO₄). Evaporation and re-dissolution of the red viscous residue in a minimum amount of CH₂Cl₂, followed by precipitation with pentane, afforded an orange powder which was chromatographed (SiO₂-H, CH₂Cl₂/hexane 9:1) to yield hexakis-adduct **24** (412 mg, 44%; see below) and **20** (280 mg, 33%), as well as mixed fractions containing **20** and **22**.

20: Orange solid. M.p. 235–245° (dec.). UV/VIS (CH₂Cl₂): 526 (1960), 387 (sh, 7020), 356 (sh, 17100), 285 (59900). IR (KBr): 2978w, 2922w, 2833w, 1747s, 1444m, 1367m, 1350s, 1290m, 1077m, 1063m, 1031m, 1011m, 854w, 753m, 707m, 661w, 590w, 538m, 528m. ¹H-NMR (400 MHz, CDCl₃): 7.07 (br. s, 8H); 6.27 (t, J = 5.3, 2H); 5.11 (br. s, 4H); 4.36 (q, J = 7.1, 4H); 4.33 (q, J = 7.1, 4H); 3.42 (d, J = 5.3, 4H); 3.05–2.90 (m, 12H); 1.34 (t, J = 7.1, 6H); 1.33 (t, J = 7.1, 6H). ¹³C-NMR (100 MHz, CDCl₃): 163.89; 163.64; 162.39; 157.96; 153.47; 147.56; 145.90; 145.68; 145.37; 145.24; 143.34; 142.50; 142.43; 141.95; 141.78; 141.57; 141.48; 138.29; 131.80; 130.20; 128.19; 125.30; 70.99; 68.47; 66.73; 62.78; 62.67; 62.36; 61.90; 53.61; 45.47; 42.43; 38.98; 34.89; 34.27; 14.16. FAB-MS: 1528.3 (12, [M + 2 O]⁺), 1512.0 (49, [M + O]⁺) (both peaks due to oxidation during sample preparation for MS), 1480.6 (100, M⁺), 1479.6 (82), 1478.7 (82).

22: ¹H-NMR (200 MHz, CDCl₃): 7.10 (br. s, 8H); 6.27 (t, J = 5.1, 2H); 5.28 (br. s, 4H); 4.45–4.15 (m, 8H); 3.44 (dd, J = 5.1, 14.0, 2H); 3.32 (dd, J = 5.1, 14.0, 2H); 3.21 (d, J = 14.2, 2H); 3.11 (d, J = 14.2, 2H); 3.05–2.90 (m, 8H); 1.45–1.20 (m, 12H).

Tetrakis(2-ethoxy-2-oxoethyl) 3',3'',6',6''-Tetrahydro-17',17''-dioxo-5',3''':5'',3''''-Bis(ethano[1,4]benzenomethanoxymethano)-3'''H, 3''''H,3''''H,3''''H-dibenzo[1,9:52,60]tricyclopropa[16,17:21,40:30,31][5,6] fullerene-C₆₀-I_h-3''''',3''''',3''''',3''''-tetracarboxylate (21) and Tetrakis(2-ethoxy-2-oxoethyl) 3',3'',6',6''-Tetrahydro-17',17''-dioxo-5',3''':5'',3''''-bis(ethano[1,4]benzenomethanoxymethano)-3'''H,3''''H,3''''H,3''''H-dibenzo[1,9:52,60]tricyclopropa[16,17:21,40:44,45][5,6]fullerene-C₆₀-I_h-3''''',3''''',3''''',3''''-tetracarboxylate (23). To a soln. of **19** (89.9 mg, 0.063 mmol) in PhCl (0.5 ml), DBU (9.5 mg, 0.063 mmol) and **17** (22.2 mg, 0.063 mmol) were added, each in PhCl (0.1 ml). The resulting mixture was stirred for 22 h at r.t., then chromatographed (SiO₂-H, CH₂Cl₂/ACOEt 100:1.5) to elute first unreacted **19** (28.1 mg, 31%), followed by the two isomeric **21** and **23**. Trace quantities of a non-characterized third compound running slightly faster than **21** were also separated. The product fractions were diluted with cyclohexane and concentrated. The precipitated solids were washed with MeOH and dried to give **21** (30.0 mg, 28%) and **23** (12.3 mg, 11%).

21: Orange solid. M.p. 195–198° (dec.). TLC (CH₂Cl₂): R_f 0.18. UV/VIS (CH₂Cl₂): 525 (1820), 491 (1860), 391 (sh, 6390), 285 (55800), 260 (sh, 51900), 244 (sh, 69300). IR (KBr): 2922w, 1750m, 1638m, 1617m, 1383m, 1260w, 1190m, 1092w, 800w. ¹H-NMR (300 MHz, CDCl₃): 7.12 (s, 8H); 6.30 (t, J = 5.1, 2H); 5.13 (br. s, 4H); 4.84 (s, 4H); 4.80 (s, 4H); 4.30–4.10 (m, 8H); 3.44 (d, J = 5.1, 4H); 3.07 (s, 4H); 3.10–2.90 (br. m, 8H); 1.28

(*t*, *J* = 7.2, 6H); 1.25 (*t*, *J* = 7.1, 6H). ^{13}C -NMR (75 MHz, CDCl_3): 166.64; 166.47; 162.88; 162.68; 162.30; 157.99; 153.51; 147.71; 145.92; 145.73; 145.44; 143.46; 142.58; 142.43; 141.98; 141.81; 141.66; 141.14; 137.84; 131.74; 130.45; 128.29 (br.); 125.27; 70.47; 68.53; 66.73; 62.44; 62.39; 62.27; 62.02; 61.92; 61.66; 61.60; 53.67; 44.22; 42.47; 38.96; 34.91; 34.22; 14.15; 14.10. MALDI-TOF-MS (DHB): 1712 (100, M^+ , $^{13}\text{C}_2^{12}\text{C}_{109}\text{H}_{58}\text{O}_{20}$), 1607 (27), 1733 (72), 1749 (29). Anal. calc. for $\text{C}_{111}\text{H}_{58}\text{O}_{20}$ (1711.67): C 77.89, H 3.42; found: C 77.71, H 4.09.

23: Orange-red solid. M.p. 190–193° (dec.). TLC (CH_2Cl_2): R_f 0.13. UV/VIS (CH_2Cl_2): 570 (1050), 548 (1210), 527 (1500), 455 (2270), 364 (sh, 11900), 302 (56800), 275 (sh, 59900), 246 (sh, 68300). IR (KBr): 2922w, 1751s, 1638w, 1618w, 1447w, 1422w, 1382m, 1289m, 1254m, 1194s, 1167m, 1092m, 1058m, 1033m, 850w, 797w, 756w, 711w, 590w, 540w, 530w. ^1H -NMR (300 MHz, CDCl_3): 7.30–7.10 (br. *m*, 8H); 6.27 (*t*, *J* = 5.1, 2H); 5.40–5.20 (br. *m*, 4H); 4.75 (*s*, 4H); 4.71 (*s*, 2H); 4.66 (*s*, 2H); 4.30–4.10 (*m*, 8H); 3.45 (*dd*, *J* = 5.1, 14.0, 2H); 3.34 (*dd*, *J* = 5.1, 14.0, 2H); 3.22 (*d*, *J* = 14.2, 2H); 3.12 (*d*, *J* = 14.2, 2H); 3.10–2.90 (br. *m*, 8H); 1.30–1.15 (*m*, 12H). ^{13}C -NMR (75 MHz, CDCl_3): 166.50; 166.46; 166.40; 163.18; 162.92; 162.33; 162.21; 155.91; 153.50; 153.39; 151.35; 146.62; 146.37; 145.87; 145.70; 145.54; 144.37; 144.15; 143.99; 143.40 (br.); 143.26; 143.21; 142.99; 142.93; 142.72; 142.52 (br.); 142.38; 142.22; 142.21; 142.07; 141.66; 137.32 (br.); 136.94; 131.76; 130.37 (br.); 128.51 (br.); 128.23 (br.); 125.23; 70.36; 68.72; 66.49; 65.99; 65.93; 62.29; 62.20; 62.10; 62.02; 61.86; 61.74; 61.57; 61.54; 61.50; 52.65; 45.99; 43.60; 42.72; 39.71; 39.28; 34.93; 34.15; 14.10; 14.04; 14.01. MALDI-TOF-MS (CCA): 1735 (10, $[M + \text{Na}]^+$, $^{13}\text{C}_2^{12}\text{C}_{109}\text{H}_{58}\text{O}_{20}\text{Na}^+$), 1712 (100, M^+ , $^{13}\text{C}_2^{12}\text{C}_{109}\text{H}_{58}\text{O}_{20}$), 1610 (8), 1545 (25). Anal. calc. for $\text{C}_{111}\text{H}_{58}\text{O}_{20}$ (1711.67): C 77.89, H 3.42; found: C 78.04, H 3.38.

Hexaethyl 3',3'',6',6''-Tetrahydro-17',17''-dioxo-5',3''',3''''-bis(ethano[1,4]benzenomethanoxymethano)-3'''H, 3'''H,3''''H,3''''H-dibenzo[1,9:52,60]tetracyclopropa[16,17:21,40:30,31:44,45][5,6]fullerene-C₆₀-I_h-3''',3'''', *3''''',3''''',3''''',3''''',3''''',3'''''-hexacarboxylate (24)*. To **12** (20.5 mg, 0.0176 mmol) in an oven-dried 10 ml flask under Ar, diethyl 2-bromopropanedioate (42.1 mg, 0.176 mmol) in dry PhCl (0.45 ml) was added, followed by DBU (26.8 mg, 0.176 mmol) in dry PhCl (0.55 ml). After 5 min, the initial suspension had turned into a homogeneous, bright-red mixture, and after stirring for 2 h more, CC (SiO_2 , CH_2Cl_2) afforded a bright-yellow soln. of **24**, which was evaporated. Subsequent recrystallization from CH_2Cl_2 /pentane gave **24** (21.1 mg, 73%). Yellow solid. M.p. > 270°. TLC (CH_2Cl_2): R_f 0.41. UV/VIS (CH_2Cl_2): 353 (sh, 21800), 332 (sh, 35000), 308 (sh, 64400), 288 (73300). IR (KBr): 2981w, 2925w, 2847w, 1746s, 1725m, 1630w, 1444w, 1384w, 1367w, 1292m, 1254s, 1217m, 1208m, 1176w, 1095w, 1065w, 1021w, 856w, 799w, 754w, 710w, 531w. ^1H -NMR (300 MHz, CDCl_3): 7.25–7.05 (br. *m*, 8H); 6.16 (*t*, *J* = 5.5, 2H); 5.22 (*s*, 4H); 4.34 (*q*, *J* = 7.1, 4H); 4.28 (*q*, *J* = 7.1, 4H); 4.24 (*q*, *J* = 7.1, 4H); 3.21 (*d*, *J* = 5.5, 4H); 3.05–2.85 (*m*, 12H); 1.35 (*t*, *J* = 7.1, 6H); 1.29 (*t*, *J* = 7.1, 6H); 1.26 (*t*, *J* = 7.1, 6H). ^{13}C -NMR (125 MHz, CDCl_3): 164.14; 163.85; 163.67; 162.99; 155.27; 155.07; 145.77; 145.41; 145.29; 144.85; 143.65; 143.36; 143.14; 142.51; 139.98; 139.73; 139.34; 139.08; 131.75; 130.24; 128.26; 125.12; 70.66; 68.56; 65.88; 62.62; 62.53; 62.42; 61.70; 61.60; 45.84; 45.52; 44.54; 42.29; 39.61; 34.84; 34.23; 14.14; 14.03; 14.00. MALDI-TOF-MS (DHB): 1658 (27, $[M + \text{Na}]^+$, $^{12}\text{C}_{110}\text{H}_{60}\text{O}_{16}\text{Na}^+$), 1636 (100, M^+ , $^{12}\text{C}_{110}\text{H}_{60}\text{O}_{16}$), 1591 (31), 1478 (35). Anal. calc. for $\text{C}_{110}\text{H}_{60}\text{O}_{16}$ (1637.70): C 80.68, H 3.69; found: C 79.87, H 3.31. X-Ray: see [39].

Hexakis(2-ethoxy-2-oxoethyl) 3',3'',6',6''-Tetrahydro-17',17''-dioxo-(5',3''',3''''-bis(ethano[1,4]benzenomethanoxymethano)-3'''H, 3'''H,3''''H,3''''H-dibenzo[1,9:52,60]tetracyclopropa[16,17:21,40:30,31:44,45][5,6]fullerene-C₆₀-I_h-3''',3'''', *3''''',3''''',3''''',3''''',3''''',3'''''-hexacarboxylate (25)*. To a soln. of **23** (60.0 mg, 0.035 mmol) in PhCl (0.5 ml), **17** (24.9 mg, 0.070 mmol) in PhCl (0.25 ml) and DBU (10.7 mg, 0.070 mmol) in PhCl (0.1 ml) were added. After stirring for 54 h, additional portions of **17** (49.8 mg, 0.14 mmol) and DBU (21.4 mg, 0.14 mmol) were each added in PhCl (0.1 ml). After an additional 21 h, the mixture was chromatographed (SiO_2 -*H*, CH_2Cl_2 /AcOEt 100:3); the yellow product fraction was diluted with cyclohexane, and concentration afforded a precipitate which was dried to give **25** (59.6 mg, 85%). Yellow solid. M.p. 232–234° (dec.). TLC (CHCl_3 /EtOH 100:1): R_f 0.09. UV/VIS (CH_2Cl_2): 355 (sh, 18200), 332 (sh, 29500), 308 (sh, 56500), 286 (69300). IR (KBr): 2993w, 1749s, 1638m, 1617m, 1383m, 1286m, 1264m, 1192s, 1094m, 1061w, 1033w, 853w, 794w, 756m, 710w, 614w, 593w, 532w. ^1H -NMR (200 MHz, CDCl_3): 7.16 (br. *s*, 8H); 6.16 (*t*, *J* = 4.9, 2H); 5.21 (br. *s*, 4H); 4.78 (*s*, 4H); 4.73 (*s*, 4H); 4.68 (*s*, 4H); 4.30–4.10 (*m*, 12H); 3.22 (*d*, *J* = 4.9, 4H); 3.10–2.85 (br. *m*, 12H); 1.35–1.15 (*m*, 18H). ^{13}C -NMR (75 MHz, CDCl_3): 166.57; 166.47; 166.39; 162.97; 162.79; 162.69; 155.26; 155.14; 145.75; 145.55; 145.46; 145.30; 143.89; 143.46; 142.51; 139.50; 139.16 (br.); 138.67; 131.69; 130.27; 128.39 (br.); 125.11; 70.21; 68.61; 65.90; 65.35; 62.31; 62.22; 62.19; 61.74; 61.62; 61.59; 61.57; 61.44; 45.56; 44.61; 43.34; 42.30; 39.36; 34.82; 34.17; 14.12; 14.04; 14.01. MALDI-TOF-MS (CCA): 2009 (34, $[M + \text{Na}]^+$, $^{13}\text{C}_2^{12}\text{C}_{120}\text{H}_{72}\text{O}_{28}\text{Na}^+$), 1986 (100, M^+ , $^{13}\text{C}_2^{12}\text{C}_{120}\text{H}_{72}\text{O}_{28}$), 1882 (18). Anal. calc. for $\text{C}_{122}\text{H}_{72}\text{O}_{28}$ (1985.90): C 73.79, H 3.65; found: C 73.28, H 3.45.

Tetrakis(2-ethoxy-2-oxoethyl) 3',3'',6',6''-Tetrahydro-17',17''-dioxo-3''''',3''''''-bis(trimethylsilyl)ethynyl-5',3''',3''''-bis(ethano[1,4]benzenomethanoxymethano)-3'''H, 3'''H,3''''H,3''''H-dibenzo[1,9:52,60]tetracyclopropa[16,17:21,40:30,31:44,45][5,6]fullerene-C₆₀-I_h-3''',3'''', *3''''',3''''',3''''',3'''''-tetracarboxylate (29)*. To a soln. of **21**

27: Yellow solid. M.p. = 250°. TLC (CH₂Cl₂/AcOEt 100:5): R_f 0.28. UV/VIS (CH₂Cl₂): 337 (sh, 155000), 312 (sh, 201000), 291 (209000), 250 (sh, 275000). IR (KBr): 2922w, 1751 s, 1638m, 1617m, 1383s, 1289w, 1253w, 1192s, 1092w, 1061w, 1033w, 853w, 799w, 777w, 711w, 539w, 534w. ¹H-NMR (300 MHz, CDCl₃): 7.16 (br. s, 24H); 6.19 (t, *J* = 5.4, 6 Hz); 5.22 (br. s, 12H); 4.77 (s, 12H); 4.71 (s, 12H); 4.24 (q, *J* = 7.2, 12 Hz); 4.20 (q, *J* = 7.2, 12 Hz); 3.25 (d, *J* = 5.4, 12 Hz); 3.10–2.85 (br. m, 36H); 1.28 (t, *J* = 7.2, 18 Hz); 1.26 (t, *J* = 7.2, 18 H). ¹³C-NMR (125 MHz, CDCl₃): 166.45; 166.43; 162.82; 162.75; 162.57; 155.97; 155.25; 145.81; 145.43; 145.39; 144.59 (br.);

144.18; 143.30 (br.); 143.15 (br.); 142.49; 139.71; 139.49; 139.12 (br.); 138.66; 131.66; 130.29; 128.32 (br.); 125.17; 88.41; 71.77; 70.42; 68.64; 67.77; 65.99; 62.26; 62.22; 61.74; 61.69; 61.63; 61.61; 45.20; 44.77; 42.34 (br.); 39.17 (br.); 34.84 (br.); 34.09 (br.); 21.19; 14.13. MALDI-TOF-MS (CCA): 5317 (9, M^+ , $C_{348}H_{174}O_{60}^+$ requires 5314), 3603 (21, 31^+ , $C_{247}H_{116}O_{40}^+$ requires 3602), 1894 (11, 32^+ , $C_{126}H_{58}O_{20}^+$ requires 1891), 1712 (100, 21^+ , $^{13}C_2^{12}C_{109}H_{58}O_{20}^+$).

26: Yellow solid. M.p. > 250°. TLC (CH_2Cl_2 /AcOEt 100:5): R_f 0.15. UV/VIS (CH_2Cl_2): 337 (sh, 202000), 311 (280000), 291 (292000), 250 (sh, 322000). IR (KBr): 2925w, 1752s, 1639w, 1619w, 1449w, 1422w, 1383m, 1289m, 1250m, 1192s, 1092m, 1061m, 1033w, 852w, 799w, 757w, 710w, 541w, 532w. 1H -NMR (300 MHz, $CDCl_3$): 7.18 (br. s, 32H); 6.17 (t, $J = 5.0$, 8H); 5.23 (br. s, 16H); 4.78 (s, 16H); 4.68 (s, 16H); 4.24 (q, $J = 7.2$, 16H); 4.17 (q, $J = 7.2$, 16H); 3.21 (d, $J = 5.0$, 16H); 3.10–2.90 (br. m, 48H); 1.29 (t, $J = 7.2$, 24H); 1.24 (t, $J = 7.2$, 24H). ^{13}C -NMR (75 MHz, $CDCl_3$): 166.47; 166.43; 162.80; 162.67; 155.78; 155.24; 145.84; 145.78; 145.55; 145.02; 144.23; 143.30; 143.22; 142.50; 139.76; 139.45; 139.11; 138.51; 131.69; 130.33; 128.36 (br.); 124.80; 75.77; 70.39; 69.49; 68.66; 68.52; 66.01; 62.32; 62.23; 61.74; 61.68; 61.63; 45.18; 44.84; 42.37; 39.26; 34.84; 34.24; 19.84; 14.14; 14.09. MALDI-TOF-MS (DHB): 5374 (2, $[M - 21]^+$, $C_{353}H_{174}O_{60}^+$ requires 5374), 3662 (11, $[M - 2 \cdot 21]^+$, $C_{242}H_{116}O_{40}^+$ requires 3662), 1952 (5, 33^+ , $C_{131}H_{48}O_{20}^+$ requires 1951), 1711 (100, 21^+ , $^{12}C_{111}H_{58}O_{20}^+$).

REFERENCES

- [1] R. Taylor, D. R. M. Walton, *Nature (London)* **1993**, 363, 685.
- [2] A. Hirsch, 'The Chemistry of the Fullerenes', Thieme Verlag, Stuttgart, 1994.
- [3] F. Diederich, C. Thilgen, *Science (Washington, D.C.)* **1996**, 271, 317.
- [4] 'Fullerene Chemistry, Tetrahedron Symposia-In-Print Number 50', Ed. A. B. Smith, III, *Tetrahedron* **1996**, 52, 4925.
- [5] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature (London)* **1990**, 347, 354.
- [6] A. Hirsch, I. Lamparth, H. R. Karfunkel, *Angew. Chem.* **1994**, 106, 453; *ibid. Int. Ed.* **1994**, 33, 437.
- [7] a) P. J. Fagan, J. C. Calabrese, B. Malone, *J. Am. Chem. Soc.* **1991**, 113, 9408; b) P. J. Fagan, B. Malone, *Acc. Chem. Res.* **1992**, 25, 134; c) A. L. Balch, D. A. Costa, J. W. Lee, B. C. Noll, M. M. Olmstead, *Inorg. Chem.* **1994**, 33, 2071; d) A. L. Balch, J. W. Lee, B. C. Noll, M. M. Olmstead, *ibid.* **1994**, 33, 5238; e) M. Rasinkangas, T. T. Pakkanen, T. A. Pakkanen, M. Ahlgren, J. Rouvinen, *J. Am. Chem. Soc.* **1993**, 115, 4901.
- [8] F. W. Tebbe, J. Y. Becker, D. B. Chase, L. E. Firment, E. R. Holler, B. S. Malone, P. J. Krusic, E. Wasserman, *J. Am. Chem. Soc.* **1991**, 113, 9900; F. N. Tebbe, R. L. Harlow, D. B. Chase, D. L. Thorn, G. C. Campbell, Jr., J. C. Calabrese, N. Herron, R. J. Young, Jr., E. Wasserman, *Science (Washington, D.C.)* **1992**, 256, 822; H. W. Kroto, R. Taylor, D. R. M. Walton, *Pure Appl. Chem.* **1994**, 66, 2091; A. G. Avent, P. R. Birkett, J. D. Crane, A. D. Darwish, G. J. Langley, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc., Chem. Commun.* **1994**, 1463;
- [9] a) J. M. Hawkins, A. Meyer, T. A. Lewis, U. Bunz, R. Nunlist, G. E. Ball, T. W. Ebbesen, K. Tanigaki, *J. Am. Chem. Soc.* **1992**, 114, 7954; b) J. M. Hawkins, A. Meyer, M. Nambu, *ibid.* **1993**, 115, 9844; c) C. C. Henderson, C. M. Rohlfing, R. A. Assink, P. A. Cahill, *Angew. Chem.* **1994**, 106, 803; *ibid. Int. Ed.* **1994**, 33, 786; d) M. Tsuda, T. Ishida, T. Nogami, S. Kurono, M. Ohashi, *J. Chem. Soc., Chem. Commun.* **1993**, 1296; e) A. Hirsch, I. Lamparth, T. Grösser, H. R. Karfunkel, *J. Am. Chem. Soc.* **1994**, 116, 9385; f) Q. Lu, D. I. Schuster, S. R. Wilson, *J. Org. Chem.* **1996**, 61, 4764; g) A. L. Balch, D. A. Costa, B. C. Noll, M. M. Olmstead, *J. Am. Chem. Soc.* **1995**, 117, 8926; h) T. Hamano, T. Mashino, M. Hirobe, *J. Chem. Soc., Chem. Commun.* **1995**, 1537; K.-D. Kampe, N. Egger, *Liebigs Ann.* **1995**, 115; X. Zhang, A. Fan, C. S. Foote, *J. Org. Chem.* **1996**, 61, 5456; i) A. L. Balch, A. S. Ginwalla, M. M. Olmstead, R. Herbst-Irmer, *Tetrahedron* **1996**, 52, 5021.
- [10] R. Breslow, *Acc. Chem. Res.* **1980**, 13, 170.
- [11] L. Isaacs, R. F. Haldimann, F. Diederich, *Angew. Chem.* **1994**, 106, 2434; *ibid. Int. Ed.* **1994**, 33, 2339.
- [12] L. Isaacs, P. Seiler, F. Diederich, *Angew. Chem.* **1995**, 107, 1636; *ibid. Int. Ed.* **1995**, 34, 1466.
- [13] C. Boudon, J.-P. Gisselbrecht, M. Gross, L. Isaacs, H. L. Anderson, R. Faust, F. Diederich, *Helv. Chim. Acta* **1995**, 78, 1334.
- [14] F. Cardullo, L. Isaacs, F. Diederich, J.-P. Gisselbrecht, C. Boudon, M. Gross, *Chem. Commun.* **1996**, 797.
- [15] E. Nakamura, H. Isobe, H. Tokuyama, M. Sawamura, *Chem. Commun.* **1996**, 1747; L. L. Shiu, K. M. Chien, T. Y. Liu, T. I. Lin, G. R. Her, T. Y. Luh, *J. Chem. Soc., Chem. Commun.* **1995**, 1159; G.-X. Dong, J.-S. Li, T.-H. Chan, *ibid.* **1995**, 1725.

- [16] J.-F. Nierengarten, V. Gramlich, F. Cardullo, F. Diederich, *Angew. Chem.* **1996**, *108*, 2242; *ibid. Int. Ed.* **1996**, *35*, 2101.
- [17] T. Grösser, M. Prato, V. Lucchini, A. Hirsch, F. Wudl, *Angew. Chem.* **1995**, *107*, 1462; *ibid. Int. Ed.* **1995**, *34*, 1343; G. Schick, A. Hirsch, H. Mauser, T. Clark, *Chem. Eur. J.* **1996**, *2*, 935.
- [18] B. Kräutler, T. Müller, J. Maynollo, K. Gruber, C. Kratky, P. Ochsenbein, D. Schwarzenbach, H. B. Bürgi, *Angew. Chem.* **1996**, *108*, 1294; *ibid. Int. Ed.* **1996**, *35*, 1204.
- [19] I. Lamparth, C. Maichle-Mössmer, A. Hirsch, *Angew. Chem.* **1995**, *107*, 1755; *ibid. Int. Ed.* **1995**, *34*, 1607; I. Lamparth, A. Herzog, A. Hirsch, *Tetrahedron* **1996**, *52*, 5065.
- [20] P. Timmerman, L. E. Witschel, F. Diederich, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Helv. Chim. Acta* **1996**, *79*, 6.
- [21] B. Kräutler, J. Maynollo, *Angew. Chem.* **1995**, *107*, 69; *ibid. Int. Ed.* **1995**, *34*, 87.
- [22] S. R. Wilson, Q. Lu, *Tetrahedron Lett.* **1995**, *36*, 5707.
- [23] P. Timmerman, H. L. Anderson, R. Faust, J.-F. Nierengarten, T. Habicher, P. Seiler, F. Diederich, *Tetrahedron* **1996**, *52*, 4925.
- [24] 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.
- [25] L. Isaacs, F. Diederich, *Helv. Chim. Acta* **1993**, *76*, 2454.
- [26] a) Y. Rubin, S. Khan, D. I. Freedberg, C. Yeretian, *J. Am. Chem. Soc.* **1993**, *115*, 344; b) P. Belik, A. Gügel, J. Spickermann, K. Müllen, *Angew. Chem.* **1993**, *105*, 95; *ibid. Int. Ed.* **1993**, *32*, 78.
- [27] B. Kräutler, M. Puchberger, *Helv. Chim. Acta* **1993**, *76*, 1626.
- [28] J. J. P. Stewart, *J. Comput. Chem.* **1989**, *10*, 209; F. Diederich, L. Isaacs, D. Philp, *J. Chem. Soc., Perkin Trans. 2* **1994**, 391.
- [29] P. Knochel, M. C. P. Yeh, S. C. Berk, *J. Org. Chem.* **1988**, *53*, 2392; b) B. H. Lipschutz, R. S. Wilhelm, D. M. Floyd, *J. Am. Chem. Soc.* **1981**, *103*, 7672.
- [30] R. L. Frank, R. P. Seven, *Org. Synth. 1955 Coll. Vol. 3*, 499; R. C. Krug, T. F. Yen, *J. Org. Chem.* **1956**, *21*, 1082; E. J. Corey, N. H. Andersen, R. M. Carlson, J. Paust, E. Vedejs, I. Viattas, R. E. K. Winter, *J. Am. Chem. Soc.* **1968**, *90*, 3245; K. J. Shea, L. D. Burke, *J. Org. Chem.* **1988**, *53*, 318.
- [31] a) F. Diederich, U. Jonas, V. Gramlich, A. Herrmann, H. Ringsdorf, C. Thilgen, *Helv. Chim. Acta* **1993**, *76*, 245; A. Herrmann, F. Diederich, C. Thilgen, H.-U. ter Meer, W. H. Müller, *ibid.* **1994**, *77*, 1689.
- [32] Y.-Z. An, G. A. Ellis, A. L. Viado, Y. Rubin, *J. Org. Chem.* **1995**, *60*, 6353.
- [33] J. W. Arbogast, A. P. Darmanyan, C. S. Foote, Y. Rubin, F. Diederich, M. M. Alvarez, S. J. Anz, R. L. Whetten, *J. Phys. Chem.* **1991**, *95*, 11; H. Tokuyama, E. Nakamura, *J. Org. Chem.* **1994**, *59*, 1135; J. L. Anderson, Y.-Z. An, Y. Rubin, C. S. Foote, *J. Am. Chem. Soc.* **1994**, *116*, 9763; M. Orfanopoulos, S. Kambourakis, *Tetrahedron Lett.* **1994**, *35*, 1945.
- [34] C. Bingel, *Chem. Ber.* **1993**, *126*, 1957.
- [35] J. A. Schluter, J. M. Seaman, S. Taha, H. Cohen, K. R. Lykke, H. H. Wang, J. M. Williams, *J. Chem. Soc., Chem. Commun.* **1993**, 972; K. Komatsu, Y. Murata, N. Sugita, K. Takeuchi, T. S. M. Wan, *Tetrahedron Lett.* **1993**, *34*, 8473.
- [36] M. El-Saidi, K. Kassam, D. L. Pole, T. Tadey, J. Warkentin, *J. Am. Chem. Soc.* **1992**, *114*, 8751.
- [37] L. Isaacs, F. Diederich, *Helv. Chim. Acta* **1993**, *76*, 2454.
- [38] W. W. Win, M. Kao, M. Eiermann, J. J. McNamara, F. Wudl, D. L. Pole, K. Kassam, J. Warkentin, *J. Org. Chem.* **1994**, *59*, 5871.
- [39] P. Seiler, L. Isaacs, F. Diederich, *Helv. Chim. Acta* **1996**, *79*, 1047.
- [40] H. Hauptmann, *Tetrahedron Lett.* **1974**, 3587.
- [41] Y.-Z. An, Y. Rubin, C. Schaller, S. W. McElvany, *J. Org. Chem.* **1994**, *59*, 2927.
- [42] a) A. de Meijere, S. Kozhushkov, C. Puls, T. Haumann, R. Boese, M. J. Cooney, L. T. Scott, *Angew. Chem.* **1994**, *106*, 934; *ibid. Int. Ed.* **1994**, *33*, 869; b) A. de Meijere, S. Kozhushkov, T. Haumann, R. Boese, C. Puls, M. J. Cooney, L. T. Scott, *Chem. Eur. J.* **1995**, *1*, 124; c) 'Modern Acetylene Chemistry', Eds. P. J. Stang and F. Diederich, VCH, Weinheim, 1995.
- [43] A. S. Hay, *J. Org. Chem.* **1962**, *27*, 3320.
- [44] O. M. Behr, G. Eglinton, A. R. Galbraith, R. A. Raphael, *J. Chem. Soc.* **1960**, 3614.
- [45] F. Diederich, Y. Rubin, C. B. Knobler, R. L. Whetten, K. E. Schriver, K. N. Houk, Y. Li, *Science (Washington, D.C.)* **1989**, *245*, 1088; Y. Rubin, C. B. Knobler, F. Diederich, *J. Am. Chem. Soc.* **1990**, *112*, 1607; Y. Rubin, M. Kahr, C. B. Knobler, F. Diederich, C. L. Wilkins, *ibid.* **1991**, *113*, 495; F. Diederich, Y. Rubin, O. L. Chapman, N. S. Goroff, *Helv. Chim. Acta* **1994**, *77*, 1441.
- [46] S. W. McElvany, M. M. Ross, N. S. Goroff, F. Diederich, *Science (Washington, D.C.)* **1993**, *259*, 1594.

- [47] Y. Tobe, T. Fujii, H. Matsumoto, K. Naemura, Y. Achiba, T. Wakabayashi, *J. Am. Chem. Soc.* **1996**, *118*, 2758; Y. Tobe, H. Matsumoto, K. Naemura, Y. Achiba, T. Wakabayashi, *Angew. Chem.* **1996**, *108*, 1924; *ibid. Int. Ed.* **1996**, *35*, 1800; G. A. Adamson, C. W. Rees, *J. Chem. Soc., Perkin Trans. 1* **1996**, 1535.
- [48] J. Anthony, A. M. Boldi, C. Boudon, J.-P. Gisselbrecht, M. Gross, P. Seiler, C. B. Knobler, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 797.
- [49] L. Isaacs, A. Wehrsig, F. Diederich, *Helv. Chim. Acta* **1993**, *76*, 1231.