

## 2. Fullerene-Acetylene Molecular Scaffolding: Chemistry of 2-Functionalized 1-Ethynylated C<sub>60</sub>, Oxidative Homocoupling, Hexakis-adduct Formation, and Attempted Synthesis of C<sub>124</sub><sup>2-</sup>

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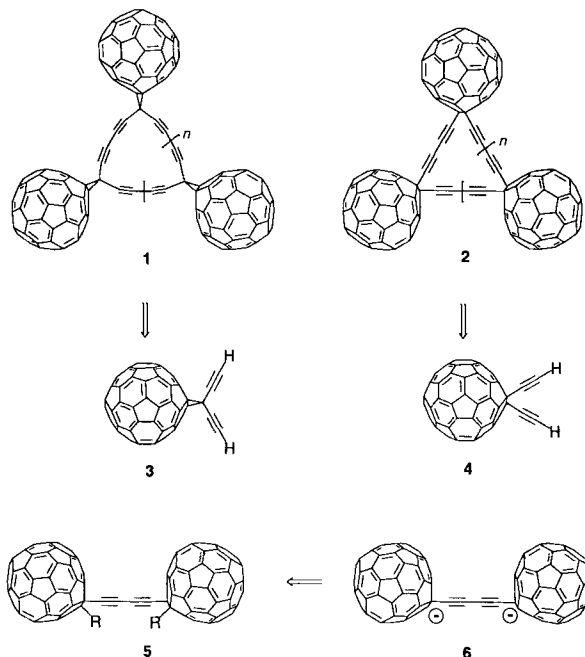
On the way to the fullerene-acetylene hybrid carbon allotropes **2** and **6**, the oxidative homocoupling of the 2-functionalized 1-ethynylated C<sub>60</sub> derivatives **11**, **12**, **14**, and **15** was investigated. Under *Glaser-Hay* conditions, the two soluble dumbbell-shaped bisfullerenes **17** and **18**, with two C<sub>60</sub> moieties linked by a buta-1,3-diynediyl bridge, were formed in 52 and 82% yield, respectively (*Scheme 2*). Cyclic-voltammetric measurements revealed that there is no significant electronic communication between the two fullerene spheres via the buta-1,3-diynediyl linker. Removal of the 3,4,5,6-tetrahydro-2*H*-pyran-2-yl (Thp) protecting groups in **18** gave in 80% yield the highly insoluble dumbbell **19** with methanol groups in the 2,2'-positions of the buta-1,3-diynediyl-bridged carbon spheres. Attempted conversion of **19** to the all-carbon dianion **6** (C<sub>124</sub><sup>2-</sup>) via base-induced elimination of formaldehyde was not successful presumably due to *exo*-dig cyclization of the formed alkoxides. The occurrence of this cyclization under furan formation was proven for 2-[4-(trimethylsilyl)buta-1,3-diyn-1-yl][60]fullerene-1-methanol (**21**), a soluble model compound for **19** (*Scheme 3*). To compare the properties of ethynylated fullerene mono-adducts to those of corresponding higher adducts, hexakis-adducts **26** and **28** with an octahedral functionalization pattern resulting from all-*e* (equatorial) additions were prepared by the reversible-template method of *Hirsch* (*Scheme 4*). Reaction of the ethynylated mono-adducts **25** or **13** with diethyl 2-bromomalonate/1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the presence of 1,9-dimethylanthracene (DMA) as reversible template led to **26** and **28** in 28 and 22% yield, respectively. Preliminary experiments indicated a significant change in reactivity and NMR spectral properties of the fullerene addends with increasing degree of functionalization.

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**1. Introduction.** – In our program targeting novel synthetic all-carbon molecules [1], we recently started combining the chemistry of fullerenes and acetylenes with the ultimate objective to prepare fullerene-acetylene hybrid carbon allotropes like **1** and **2** (*Scheme 1*) [2]. These structures have in common a central acetylenic framework that is sterically shielded by fullerene 'end-caps'. Similar acetylenic macrocycles were reported [1] [3], but the combination with fullerenes as 'end-capping' groups avoids the incorporation of any elements other than carbon, thus providing access to new families of carbon allotropes.

In a series of earlier papers [2], we reported the synthesis of diethynylmethano-fullerene **3** [4] and its oxidative homo- and heterocoupling reactions under *Glaser-Hay* conditions, which resulted in the formation of the first dumbbell-type bisfullerene molecule soluble enough for full spectroscopic characterization, including X-ray crystallography [2c]. All-carbon molecules **1** (*n* = 1, 2, ...) could not be isolated from oxidative cyclizations of **3**, presumably due to their extremely low solubility. In contrast, cyclo-oligomerizations of a diethynylmethano-functionalized C<sub>60</sub> hexakis-adduct afforded soluble derivatives of the cyclic oligomers **1** (with *n* = 1 and 2) as the major products [5].

Scheme 1. Synthetic Approaches to Fullerene-Acetylene Hybrid Carbon Allotropes

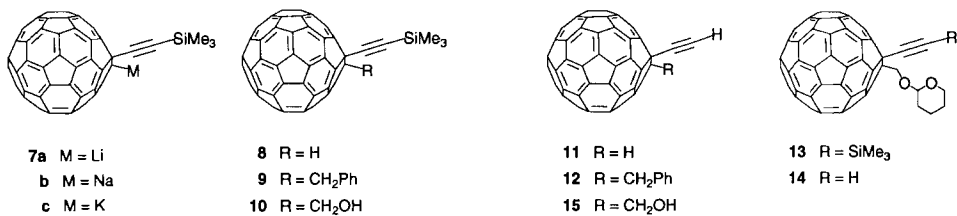


By analogy, oxidative cyclization of 1,2-diethynyl[60]fullerene **4** should potentially give access to **2**, another family of fullerene-acetylene hybrid allotropes. As a result of the smaller angle between the two alkyne groups in **4** (as compared to **3**), we expected dimeric fullerene **2** ( $n = 0$ ), a compound that might have enough solubility for isolation and spectroscopic characterization, to be the major product from the cyclo-oligomerization of **4**.

Since the synthesis of 1,2-diethynyl[60]fullerene **4** has proven to be unexpectedly difficult [2c], a number of 2-functionalized 1-ethynyl[60]fullerenes were prepared as model systems for **4** [2c]. These compounds could serve as starting materials for the synthesis of dumbbell-shaped **5** [6] and ultimately, if addend R (in **5**) is a removable group, of the all-carbon dianion **6** ( $C_{124}^{2-}$ ). In this paper, we report on the synthesis and electrochemical properties of buta-1,3-diyne-linked bis(fullerenes) **5** and their attempted conversion into dianion **6**. To analyze the electronic contributions of the fullerene sphere to the unusual reactivity that was observed for some of the addends in 2-functionalized 1-ethynyl[60]fullerenes [2c], we prepared fullerene hexakis-adducts containing these addends by the reversible-template method recently introduced by *Hirsch* and coworkers [7]. The one-step conversion of ethynylated fullerene mono-adducts into the corresponding hexakis-adducts will also be described.

**2. Results and Discussion.** – 2.1. *Synthesis of 2-Functionalized 1-Ethynylfullerenes.* The (trimethylsilyl)ethynyl derivatives **8–10** were prepared by reacting C<sub>60</sub> with lithium (trimethylsilyl)acetylide in toluene/THF followed by quenching the formed Li<sup>+</sup> salt **7a**

with the appropriate electrophile [2a,c] [8]. However, for reasons of easier product purification, a slightly modified protocol was preferable for the synthesis of **8** and **9**. As reported, alcohol **10** could be converted quantitatively to the Na<sup>+</sup> salt **7b** by treatment with NaH in THF [2c]. Quenching of the solution with AcOH afforded 1,2-dihydro-2-[(trimethylsilyl)ethynyl][60]fullerene **8** in quantitative yield. This procedure avoided the severe difficulties encountered with the purification of the highly lipophilic **8** from larger amounts of unreacted C<sub>60</sub> in the direct preparation method. In the modified procedure, this separation was readily achieved at the stage of alcohol **10** which differs substantially in its polarity from the unreacted fullerene. In a similar way, benzyl derivative **9** was obtained in 48% yield after treatment of a solution of **7b** (prepared from **10**) in THF with benzyl bromide at reflux for 2 h. To our surprise, a small amount of C<sub>60</sub> was present in the final product, indicating that the addition of sodium (trimethylsilyl)acetylide was reversible at this temperature. However, formation of C<sub>60</sub> was not observed, when a solution of **7b** was refluxed for 2 h in the absence of benzyl bromide. Reaction of **7b** with benzyl bromide at room temperature was very slow and the yield very low.



Removal of the Me<sub>3</sub>Si protecting groups in compounds **8** and **9** was achieved by proto-desilylation (K<sub>2</sub>CO<sub>3</sub>, THF/MeOH), either at reflux (**8**) or at room temperature (**9**), to give the corresponding ethynyl derivatives **11** and **12**, respectively. Alcohol **10** was not stable under these conditions and, in the absence of O<sub>2</sub>, readily extruded formaldehyde to give K<sup>+</sup> salt **7c**. Therefore, alcohol **10** was converted in 82% yield to the corresponding chiral 3,4,5,6-tetrahydro-2*H*-pyran-2-yl (Thp) ether **13** by treatment with a large excess of 3,4-dihydro-2*H*-pyran (Dhp)/pyridinium *p*-toluenesulfonate (PPTS) [9] in refluxing THF. Apart from serving as a protecting group, the Thp moiety also raised the solubility of the compound. *E.g.*, **13** is highly soluble in CH<sub>2</sub>Cl<sub>2</sub>, in which **8** is only poorly soluble.

The <sup>1</sup>H-NMR spectrum of **13** showed, among other characteristic signals, two *d*'s at 5.64 and 5.52 ppm for the diastereotopic protons of the CH<sub>2</sub> group directly attached to the fullerene. The C<sub>1</sub> symmetry of **13** is supported by the observation of 53 out of 60 expected fullerene resonances (51 between 154 and 134 ppm; 2 at 65.79 and 58.83 ppm) in the <sup>13</sup>C-NMR spectrum.

Removal of the Me<sub>3</sub>Si protecting group in **13** by proto-desilylation (K<sub>2</sub>CO<sub>3</sub>, MeOH) afforded Thp-protected **14** in 89% yield. Apparently, two conformers of the six-membered Thp ring of **14** are populated (<sup>13</sup>C-NMR), and their interconversion is slow on the NMR time scale, presumably due to steric interactions with the surrounding fullerene and alkyl groups.

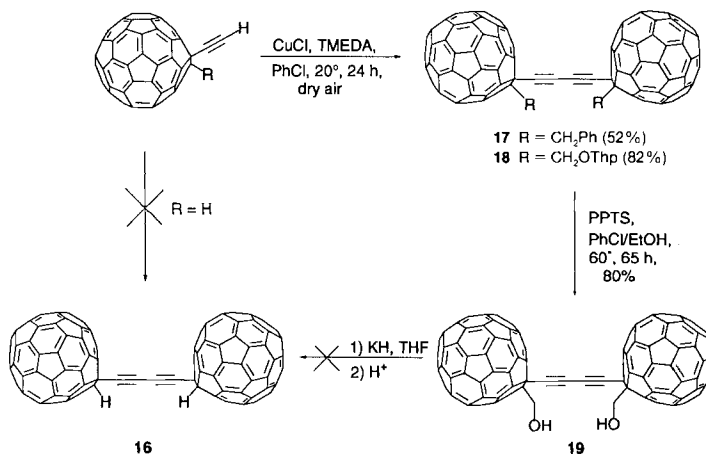
The <sup>1</sup>H-NMR spectrum of **14** displays the characteristic *s* at 3.00 ppm for the terminal acetylene proton, and its <sup>13</sup>C-NMR spectrum shows a total of 54 out of 60 fullerene resonances (52 between 154 and 134 ppm; 2 at 65.77 and 57.49 ppm) expected for a C<sub>1</sub>-symmetrical compound. Double resonances are observed for both the stereogenic (99.40 and 99.34 ppm) and the terminal acetylenic (72.89 and 72.85 ppm) C-atoms.

The Thp protecting group was removed by heating a solution of **14** in PhCl/EtOH 10:1 to 60° in the presence of PPTS for 40 h [9], giving the stable alcohol **15** in 95% yield. The  $C_3$ -symmetrical compound is reasonably well soluble in PhCl, and  $CS_2$ , but virtually insoluble in any other common organic solvent.

The  $^1H$ -NMR spectrum of **15** in  $CDCl_3/CS_2$  3:1 shows the characteristic *d* at 5.68 ppm and *t* at 3.82 ppm for the  $CH_2OH$  group as well as a *s* at 3.17 ppm for the  $\equiv CH$  proton. The  $^{13}C$ -NMR spectrum confirms the  $C_3$  symmetry showing 31 (29 between 153 and 134 ppm; 2 at 69.00 and 53.47 ppm) of the 32 expected fullerene resonances.

2.2. *Oxidative Homocoupling Reactions of 2-Functionalized 1-Ethynylfullerenes.* Diethynylmethanofullerenes such as **3** reacted smoothly under *Glaser-Hay* conditions (CuCl, *N,N,N',N'*-tetramethylethylenediamine (TMEDA), dry air) to give both homo- and hetero-coupled buta-1,3-diynes, without affecting the fullerene core [2]. However, all efforts to directly homocouple ethynylfullerenes **11** and **15** to give the hydro-substituted derivative **16** ( $C_{124}H_2$ ) or dimethanol **19** ( $C_{126}H_6O_2$ ), respectively, failed, and soluble products could not be isolated (*Scheme 2*). Model studies with **8** and **10** demonstrated that the failure of **11** and **15** to give the expected butadiynes was not related to the coupling step but rather due to the instability of the fullerene anions, that form under the slightly basic reaction conditions, against oxidation by the  $O_2$  present. We, therefore, studied the homocoupling of ethynylfullerenes **12** and **14**, carrying base-stable substituents at their 2-position. *In situ* preparation of the *Hay* catalyst [10] in PhCl in the presence of **12** followed by stirring for 24 h in dry air at room temperature afforded bisfullerene **17** in 52% yield. The compound was readily soluble in PhCl and  $CS_2$ , and complete spectroscopic characterization was obtained.

Scheme 2. *Oxidative Homocoupling under Glaser-Hay Conditions to Give Dumbbell-Shaped Bis(fullerenes)*



Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry in the negative-ion mode provides conclusive evidence for the dimeric structure of **17** with the molecular-ion peak appearing as parent ion at  $m/z$  1670.8 ( $^{13}C^{12}C_{137}H_{14}$  requires 1671.1). The  $^1H$ -NMR spectrum shows the expected resonances for the Ph groups between 7.46 and 7.15 ppm together with a *s* at 5.20 ppm for the benzylic protons. The 31 fullerene resonances (29 between 154 and 134 ppm; 2 at 66.64 and 60.69 ppm) in the  $^{13}C$ -NMR spectrum clearly indicate the

$C_2$  symmetry of the compound. A comparison between the UV/VIS spectra of dimeric **17** and monomeric **9** [2c] reveals similar absorption bands and nearly identical end absorptions at  $\lambda$  698 nm, suggesting that there is little or no electronic interaction between the two fullerene moieties in **17**. These findings were confirmed in the electrochemical studies described below.

Homocoupling of Thp-protected **14** gave bisfullerene **18** in 82% yield as a mixture of three stereoisomers, a racemate ( $R,R/S,S$ ) and one *meso* ( $R,S$ ) form, as could be concluded from the 500-MHz  $^1\text{H-NMR}$  spectrum. Interestingly, in the MALDI-TOF mass spectrum a fragmentation peak was found at  $m/z$  744.4, which possibly could correspond to the formation of dianion **6** ( $^{13}\text{C}^{12}\text{C}_{123}^{2-}$  requires 744.4).

The  $^1\text{H-NMR}$  spectrum (500 MHz) of **18** shows two  $d$ 's of equal intensity at 5.43 ppm ( $\Delta\delta = 0.005$  ppm) for one of the two diastereotopic methylene protons of the protected alcohol group. Since the two fullerene spheres in each stereoisomer are interconvertible through symmetry operations (mirror plane in the *meso* form and  $C_2$  axis in the racemate), a total of 120 fullerene resonances is expected in the  $^{13}\text{C-NMR}$  spectrum. However, only 52 resonances (50 between 154 and 134 ppm; 2 at 66.45 and 57.96 ppm) are found together with only 2 resonances at 78.79 and 69.02 ppm for the butadiynediyl C-atoms, which indicates that most of the resonances of racemic and *meso*-forms are not resolved. MALDI-TOF mass spectrometry gives final proof for the dimeric structure of **18**, exhibiting the molecular ion peak at  $m/z$  1718.0 ( $^{13}\text{C}^{12}\text{C}_{135}\text{H}_{22}\text{O}_4$  requires 1719.2).

**2.3. Electrochemical Studies.** The electrochemical behavior of bisfullerenes **17** and **18** was studied by cyclic voltammetry (CV) and compared to that of monofullerenes **9** and **13** to determine the extent of electronic interaction between the butadiynediyl-connected fullerene spheres. The measurements were performed in  $\text{PhCl}/\text{CH}_2\text{Cl}_2$  1:1 with 0.1M  $(\text{Bu}_4\text{N})\text{PF}_6$  as the supporting electrolyte. The data (Table) clearly indicated that all compounds have the same redox potentials (vs. the ferrocene/ferricinium couple ( $\text{Fc}/\text{Fc}^+$ )) within the experimental precision. Peak currents for the bisfullerenes were about twice those of the corresponding monofullerenes which is indicative of a two-electron process for each bisfullerene reduction step. All studied species were reduced in three

Table. Formal Reduction Potentials (in V vs.  $\text{Fc}/\text{Fc}^+$ ) from Cyclic Voltammetry of Monofullerenes **9** and **13** and Bisfullerenes **17** and **18** on a Glassy Carbon Electrode in  $\text{PhCl}/\text{CH}_2\text{Cl}_2$  1:1 (+ 0.1M  $\text{Bu}_4\text{NPF}_6$ )

	Reduction Potentials		
	$E_1$	$E_2$	$E_3$
<b>9</b>	-1.12	-1.49	-2.01
<b>13</b>	-1.12	-1.49	-2.01
<b>17</b>	-1.12	-1.48	-2.01
<b>18</b>	-1.10	-1.46	-1.99

reversible reduction steps [11] [12], the peak potential difference being close to 70 mV at a scan rate of 0.1 V/s (uncorrected for ohmic drop). The peak shapes in the cyclic voltammograms (Fig.) clearly indicated that the two  $\text{C}_{60}$  moieties in **17** and **18** are independent [13]. Also, the voltammograms recorded on a RDE (rotating disk electrode) gave well defined waves, whose slopes were close to 60 mV, as expected for a reversible one-electron charge transfer. Again, the slopes of 60 mV demonstrate that the two fullerene redox centers in **17** and **18** are independent [14].

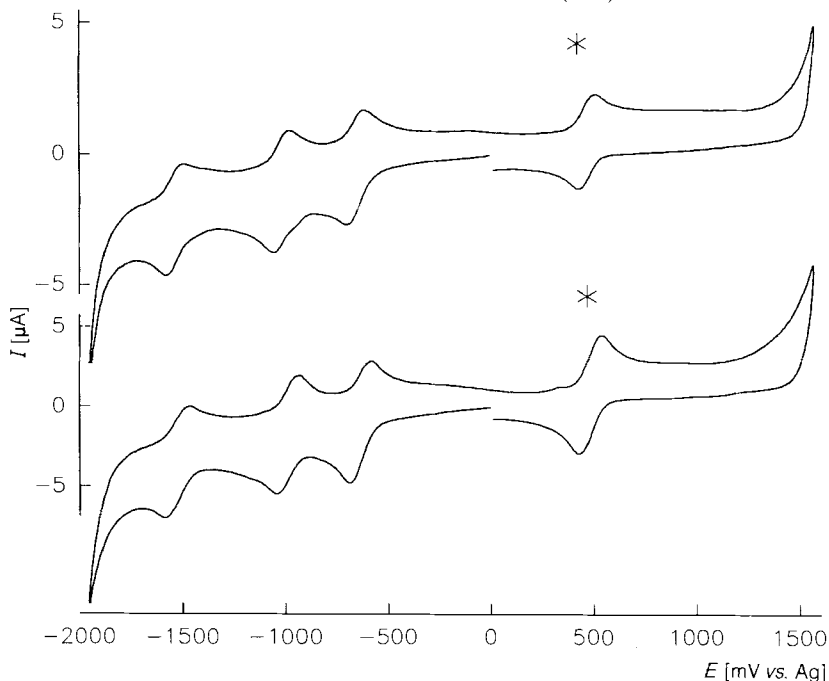
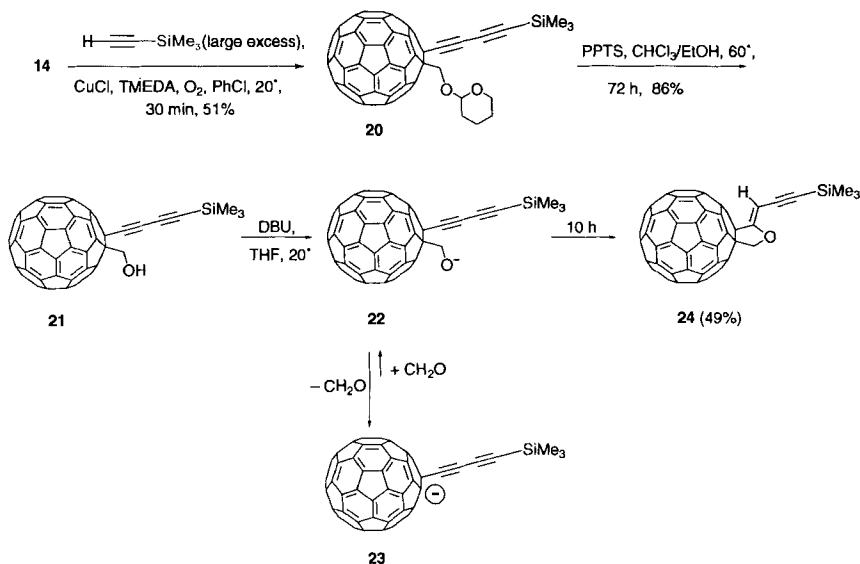


Figure. Cyclic voltammograms (top) of monofullerene **9** ( $c = 1.65 \cdot 10^{-4} \text{ M}$ ) and (bottom) of bisfullerene **17** ( $c = 1.5 \cdot 10^{-4} \text{ M}$ ) in  $\text{PhCl}/\text{CH}_2\text{Cl}_2$  1:1 (+ 0.1M  $(\text{Bu}_4\text{N})\text{PF}_6$ ) recorded on a glassy carbon electrode. Scan rate 0.1 V/s. \* Refers to the  $\text{Fc}/\text{Fc}^+$  couple used as internal standard.

2.4. *Attempted Synthesis of  $\text{C}_{124}^{2-}$* . The planned route to dianion **6** ( $\text{C}_{124}^{2-}$ ) involved removal of the Thp protecting group in **18** to give diol **19** and subsequent base-induced elimination of formaldehyde [2c]. Deprotection of **18** was carried out with PPTS in  $\text{PhCl}/\text{EtOH}$  10:1 under high dilution (0.015mM) to prevent product precipitation and afforded diol **19** in 80% yield. The shiny black crystals were completely insoluble in any solvent other than 1,2-dichlorobenzene and 1-methylnaphthalene and, as a consequence, no NMR spectroscopic studies could be performed. The identity of **19** was best proven by MALDI-TOF mass spectrometry which showed the molecular ion as parent ion at  $m/z$  1550.8 ( $^{13}\text{C}_{125}\text{H}_6\text{O}_2$  requires 1551.0).

In an attempted preparation of dianion **6** ( $\text{C}_{124}^{2-}$ ) by treatment of diol **19** with KH in THF, we did not obtain the green solution which is highly characteristic for fullerene mono-anions [15]. Instead a dark brown mixture formed which contained only products too insoluble for characterization. As a model reaction, we subsequently studied the behavior of the soluble butadiyne **21** under basic conditions. To prepare **21**, Thp-protected ethynylfullerene **14** was coupled with (trimethylsilyl)acetylene (large excess) under *Glaser-Hay* conditions to give **20** in 51% yield (*Scheme 3*). Deprotection of **20** (PPTS,  $\text{CHCl}_3/\text{EtOH}$ , 60°) afforded alcohol **21** (86% yield).

In the  $^{13}\text{C}$ -NMR spectrum of  $\text{C}_1$ -symmetrical **20**, 54 of the expected 60 fullerene resonances (52 between 154 and 134; 2 at 66.91 and 58.07 ppm) were observed and the four signals at 88.20, 87.78, 76.85, and 68.89 ppm clearly proved the presence of the butadiyne moiety. The  $\text{C}_s$ -symmetrical **21** displayed 31 of the expected 32  $^{13}\text{C}$ -NMR fullerene resonances, 29 between 153 and 134 and two at 70.14 and 53.47 ppm.

Scheme 3. Formation of Alcohol **21** and Conversion into Furan **24** by *exo-dig* Cyclization of Alkoxide **22**

When alcohol **21** was treated with DBU (1.2 equiv.) in THF at 0°, initial formation of the corresponding fullerene anion **23** by loss of formaldehyde was observed, according to the immediate color change from dark brown to green (Scheme 3). However, the anion turned out to be unstable at this temperature as the color of the solution gradually changed from green to brown within 1 h. TLC Analysis revealed the formation of a new compound which could be isolated in 49% yield after flash chromatography ( $R_f$  0.3 in cyclohexane). It was characterized as furan **24**, based on the MALDI-TOF spectrum ( $M^-$  at  $m/z$  872.3 ( $\text{C}_{68}\text{H}_{12}\text{OSi}$  requires 872.0)) and the  $^1\text{H-NMR}$  spectrum (6.02 and 5.85 (2s,  $\text{CH}_2$  and olef. H, resp.) and 0.32 ppm (s,  $\text{Me}_3\text{Si}$ );  $^{13}\text{C-NMR}$ : 166.05 and 85.96 ppm (olef.  $\text{C}=\text{C}$ )). Formation of **24** most probably occurred *via* *exo-dig* cyclization of alkoxide anion **22**, which is in equilibrium with fullerene anion **23** *via* reaction with the initially extruded formaldehyde. Related cyclizations were observed for *ortho*-ethynylated naphthalenols [16a] and phenols [16b, c].

We are currently investigating alternative routes, which include trapping the initially formed formaldehyde, for the clean conversion of alcohol **21** into anion **23** and, ultimately, of diol **19** into dianion **6** ( $\text{C}_{124}^{2-}$ ).

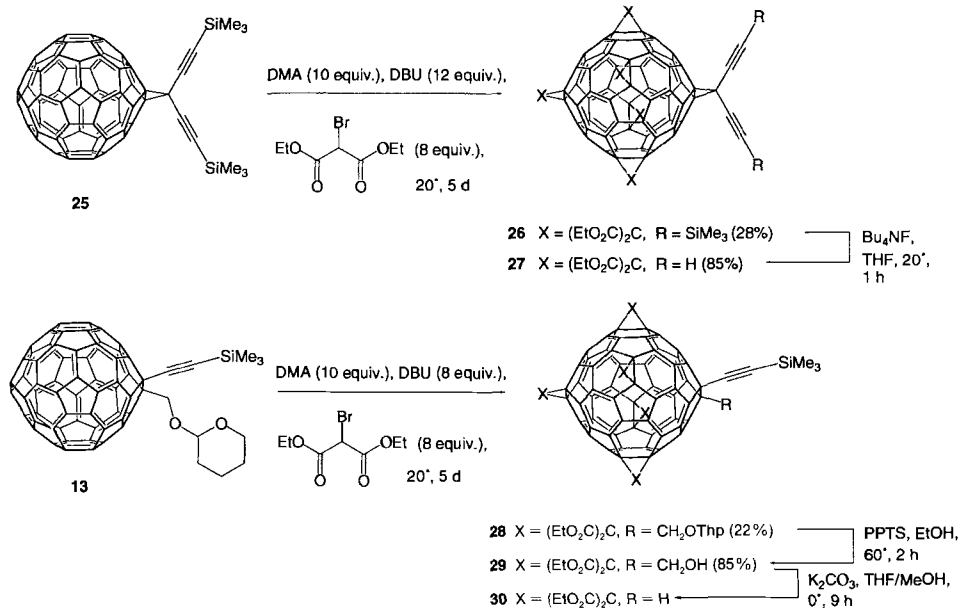
2.5. *One-Step Reversible-Template Mediated Synthesis of Ethynyl-Functionalized Hexakis-adducts of  $\text{C}_{60}$* . Some of the 2-functionalized 1-[(trimethylsilyl)ethynyl][60]fullerene derivatives prepared so far showed quite unusual reactivities [2c], *e.g.* the rapid conversion of alcohol **10** into the corresponding fullerene anion **7** upon treatment with base (*vide supra*). This and similar reactions [2c] are driven by the very high stability of the forming fullerene mono-anions [15b] and have severely hampered our efforts to prepare 1,2-diethynyl[60]fullerene **4**. We became interested in exploring whether this characteristic reactivity is maintained at the stage of  $\text{C}_{60}$  hexakis-adducts [5] [7] [17], which have a greatly reduced conjugated  $\pi$ -chromophore [11] and, therefore, should form significantly less stable mono-anions.

For a rapid access to  $C_{60}$  hexakis-adducts incorporating alkynyl groups such as in **3** or **8–15**, we applied the reversible-template method recently described by Hirsch and coworkers [7]. In this procedure, 1,9-dimethylantracene (DMA) is used as a template which undergoes reversible *Diels-Alder* additions with the fullerene. After addition to the fullerene, the template directs diethyl malonate addends in the *Bingel* reaction [18] regioselectively into equatorial (e) positions, ultimately yielding a hexakis-malonate adduct with an octahedral, all-e addition pattern, besides free template. The reversible-template method was shown in one example to give hexakis-adducts starting from a fullerene mono-adduct [7].

Reaction of bis[(trimethylsilyl)ethynyl]methano[60]fullerene **25** [2c] with diethyl 2-bromomalonate and DBU (8 and 12 equiv., resp.) in toluene in the presence of DMA (10 equiv.) for 5 days at room temperature produced the yellow hexakis-adduct **26**, which was isolated by flash chromatography (2 $\times$ ) in 28% yield (*Scheme 4*). In the absence of the template, hexakis-adduct **26** was obtained in only 12% yield as an inseparable 1:1 mixture with an incompletely characterized red-orange pentakis-adduct. The spectroscopic data of yellow **26** fully supported the assignment of a  $C_{2v}$ -symmetrical all-e hexakis-adduct structure [5].

The  $^1\text{H-NMR}$  spectrum (500 MHz,  $\text{CDCl}_3$ ) of **26** shows a *s* at 0.18 ppm for the  $\text{Me}_3\text{Si}$  protons together with four *t*'s around 1.30 ppm, one with double intensity, for the  $\text{MeCH}_2\text{O}$  protons, while the  $\text{MeCH}_2\text{O}$  region is not well resolved. In the carbonyl region of the  $^{13}\text{C-NMR}$  spectrum, all four expected signals are observed (163.84, 163.82, 163.79, and 163.77 ppm). However, the fullerene  $\text{sp}^2\text{-C-atom}$  region of the spectrum is not well resolved, displaying only 9 of the expected 12 resonances (4 between 146.0 and 145.7 ppm; 5 between 141.7 and 141.0 ppm). Five fullerene  $\text{sp}^3\text{-C-atom}$  resonances are observed, one at 73.21 ppm for the C-atoms carrying the diethynyl-methano bridge, which is only 2.4 ppm upfield from the corresponding resonance in mono-adduct **25**, and four

Scheme 4. Reversible-Template-Mediated Synthesis of Ethynylated Hexakis-adducts of  $C_{60}$





between 69.20 and 68.90 ppm for the C-atoms connected to the malonate bridges. Finally, the three signals at 45.36, 45.23, and 44.78 ppm represent the bridging C-atoms of the malonate esters, whereas the resonance at 21.34 ppm is characteristic for the bridging C-atom of the diethynylmethano addend.

Beside the molecular-ion peak at  $m/z$  1718.3 (14%) ( $[^{13}\text{C}^{12}\text{C}_{105}\text{H}_{68}\text{O}_{20}\text{Si}_2 + \text{H}]$  requires 1718.4), the FAB mass spectrum of **26** shows an interesting fragmentation pattern ( $m/z$  1511.0 (44), 1352.5 (31), 1194.4 (17), 1036.4 (14), 878.1 (11), 720.0 (100)) corresponding to initial loss of the diethynylmethano addend followed by consecutive losses of five malonate groups. This confirms previous findings by *Isaacs et al.* [5b] that the diethynylmethano group is bound less tightly to the fullerene core than the malonate addends and, therefore, splits off first under mass-spectrometric conditions. The IR and UV/VIS spectra of **26** resemble those measured previously for other hexakis-adducts [5].

Removal of the  $\text{Me}_3\text{Si}$  protecting groups in **26** under the proto-desilylation conditions ( $\text{K}_2\text{CO}_3$ ,  $\text{MeOH/THF}$ ) applied to the deprotection of fullerene mono-adducts was slow and low-yielding. However, using tetrabutylammonium fluoride ( $\text{Bu}_4\text{NF}$ ) on  $\text{SiO}_2$  in anhydrous THF [5b] gave diethynylmethanofullerene **27** in high yield. When *Rubin* and coworkers applied  $\text{Bu}_4\text{NF}$  to deprotect **25**, mainly decomposition and polymerization occurred [4], which illustrates the differences in reactivity between mono- and hexakis-adducts of  $\text{C}_{60}$ .

The formation of **27** was supported by the absence of the  $\text{Me}_3\text{Si}$  signal and the presence of a sharp  $\equiv\text{CH}$  s at 2.54 ppm in the  $^1\text{H-NMR}$  spectrum. In contrast to  $\text{Me}_3\text{Si}$ -protected **26**, compound **27** gave a nicely resolved  $^{13}\text{C-NMR}$  spectrum exhibiting all 12 expected fullerene  $\text{sp}^2\text{-C}$ -atom resonances (6 between 146.0 and 145.5 ppm; 6 between 141.6 and 141.0 ppm).

Reaction of **13** under similar conditions (DMA (10 equiv.), diethyl 2-bromomalonate (8 equiv.), DBU (8 equiv.)) as used for the synthesis of **26**, gave hexakis-adduct **28** in 22% yield as a yellow solid after recrystallization from  $\text{AcOEt/cyclohexane}$ . Upfield shifts in the  $^1\text{H-NMR}$  spectrum of **28** as compared to **13** are readily explained by the complete absence of pentagons with local paramagnetic ring currents [19] in the hexakis-adduct in which the  $\pi$ -chromophore is reduced to that of a fully benzenoid 'cubic cyclophane' [11] [17]. The observed changes in the  $^1\text{H-NMR}$  chemical shift parallel the changes in color and electrochemical properties which occur as a result of increasing functionalization of the carbon sphere [5] [11].

The FAB mass spectrum of **28** shows the molecular ion and, as the most intensive peak besides the  $\text{C}_{60}^+$  ion, a fragment ion at  $m/z$  1622.6 ( $[^{13}\text{C}^{12}\text{C}_{105}\text{H}_{70}\text{O}_{22}\text{Si-OThp}]$  requires 1623.3), which corresponds to the loss of an OThp fragment from the molecular ion. The  $^1\text{H-NMR}$  spectrum exhibits the characteristic two  $d$ 's for the diastereotopic protons of the protected alcohol group at 4.84 and 4.74 ppm, *ca.* 0.8 ppm upfield from their positions in mono-adduct **13**. The  $\text{Me}_3\text{Si}$  protons in **28** are also shifted upfield by 0.22 ppm as compared to **13**. The  $\text{sp}^2\text{-C}$ -atom region of the  $^{13}\text{C-NMR}$  spectrum of  $\text{C}_1$ -symmetrical **28** displays 8 (out of 10)  $\text{C}=\text{O}$  signals and 44 (out of 48) fullerene  $\text{sp}^2\text{-C}$ -atom resonances. A preliminary analysis of the  $\text{sp}^3\text{-C}$ -atom region of the spectrum suggests that the fullerene  $\text{sp}^3\text{-C}$ -atoms carrying the (trimethylsilyl)ethynyl and the protected primary alcohol groups appear at 55.78 and 40.43 ppm, which represents remarkable upfield shifts of 10.0 and 18.4 ppm from the respective resonances in mono-adduct **13**.

Cleavage of the Thp ether in **28** with PPTS in EtOH gave alcohol **29** in 85% yield. A comparison of the fullerene  $\text{sp}^2\text{-C}$ -atom resonances of **26** and **29** in the  $^{13}\text{C-NMR}$  spectrum demonstrates significant differences between the two types of hexakis-adducts. Whereas the nine signals in **26** group together in two very tight regions (146.0–145.7 and 141.7–141.0 ppm), the observed 24 fullerene  $\text{sp}^2\text{-C}$ -atom resonances in  $\text{C}_s$ -symmetrical **29**

appear over a broad range between 151.7 and 139.0 ppm, very similar to the respective resonances in the corresponding mono-adduct **10**. The origin of these significant spectral differences between hexakis-adducts **26** and **29** is unknown at present.

The FAB mass spectrum of **29** depicts the molecular ion as parent ion at  $m/z$  1639.0 ( $^{13}\text{C}^{24}\text{C}_{100}\text{H}_{62}\text{O}_2\text{Si}$  requires 1639.4). The  $^1\text{H}$ -NMR spectrum exhibits diagnostic signals for the primary alcohol group (a  $d$  at 4.87 and a  $t$  at 3.71 ppm) which appear 0.8 and 0.5 ppm upfield from their respective positions in mono-adduct **10** [2c]. In analogy to the findings for **27**, a preliminary analysis of the  $^{13}\text{C}$ -NMR spectrum again suggests large upfield shifts for the fullerene  $\text{sp}^3$ -C-atoms carrying the (trimethylsilyl)ethynyl and the primary alcohol groups: their resonances at 54.79 and 40.51 ppm appear 15.0 and 17.3 ppm upfield from the respective positions in **10**.

Preliminary experiments showed that alcohol **29** is not very stable under basic conditions; it slowly eliminated formaldehyde upon treatment with  $\text{K}_2\text{CO}_3$  in THF/EtOH at  $0^\circ$  for several hours to give hydrofullerene **30**. The corresponding reaction of mono-adduct **10** was much faster, presumably due to the much higher stability of the developing fullerene anion. In addition to this, elimination of the (trimethylsilyl)acetylide moiety in **30** was observed after prolonged reaction times, leading to the formation of the  $\text{C}_{2v}$ -symmetrical red-orange all- $e$ - $\text{C}_{60}(\text{C}(\text{CO}_2\text{Et})_2)_5$  pentakis-adduct [17a].

Attempts to prepare hexakis-adducts **29** and **30** directly from the corresponding mono-adducts **8** and **10** by the reversible-template method were unsuccessful, presumably due to the lability of both starting materials and products under basic conditions.

**3. Conclusions.** – Oxidative homocoupling of 2-functionalized 1-ethynyl[60]fullerenes provided access to a new class of butadiynediyl-linked dumbbell-shaped bisfullerenes. Electrochemical studies demonstrated complete absence of electronic interactions between the two fullerene spheres in these molecules. Attempts to convert bisfullerene-dimethanol **19** into the all-carbon dianion  $\text{C}_{124}^{2-}$  by elimination of formaldehyde with a strong base revealed that fullerenes with primary alkoxide functions adjacent to butadiynyl residues are not stable under the reaction conditions. Model studies demonstrated that the corresponding primary alkoxides cyclize in an *exo*-dig fashion, leading to the formation of furans. A series of ethynylated hexakis-adducts was prepared by the reversible-template-mediated, regioselective multiple malonate-addition sequence introduced by Hirsch and coworkers [7]. This allowed a comparison of the properties of fullerene functional groups in hexakis-adducts to those in the corresponding mono-adducts. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra displayed large differences in chemical shift for comparable resonances in the two types of adducts. Preliminary experiments with hexakis-adduct **29** showed that the chemical reactivity of functional groups also changes with increasing degree of addition. The diverse information gained in the present work on the reactivity of ethynylated fullerenes should help in the future to circumvent the obstacles encountered so far in attempts to synthesize 1,2-diethynyl[60]fullerene (**4**) and the all-carbon dianion  $\text{C}_{124}^{2-}$  and thus facilitate access to new families of all-carbon molecules via fullerene-acetylene molecular scaffolding.

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## Experimental Part

**General.** All reactions were performed in standard glassware under an inert atmosphere (N<sub>2</sub> or Ar). THF was freshly distilled from sodium benzophenone ketyl. The 3,4-dihydro-2H-pyran was fractionally distilled before use. PhCl was dried over molecular sieves (4 Å) for several days before use. All other solvents were used without further purification. Reagents were reagent-grade commercials. Degassing of solvents was performed by repetitive freeze-pump-thaw cycles. Evaporation and concentration *in vacuo* was done at water aspirator pressure; drying *in vacuo* at 10<sup>-2</sup> Torr. Column chromatography and flash chromatography (FC): *E. Merck* silica gel 60 (230–240 mesh, 0.040–0.063 mm) and silica gel *H* from *Fluka*. Thin-layer chromatography (TLC): plastic sheets pre-coated with silica gel *G UV<sub>254</sub>* from *Macherey-Nagel*; visualization by UV light. Melting points: *Büchi Smp-20*; uncorrected. UV/VIS Spectra: *Varian Cary-5* spectrophotometer;  $\lambda_{\max}$  in nm ( $\epsilon$ ). IR Spectra (cm<sup>-1</sup>): *Perkin-Elmer 1600-FTIR*. NMR Spectra: *Bruker AM 500* (<sup>13</sup>C) and *Varian Gemini 300* or *200* (<sup>1</sup>H) at 296 or 300 K, with solvent peaks or SiMe<sub>4</sub> as reference. MALDI-TOF MS (*m/z* (%)): *Bruker REFLEX* spectrometer with 2,5-dihydroxybenzoic acid (DHB), 1,8,9-anthracenetriol (ATO), or  $\alpha$ -cyano-4-hydroxycinnamic acid (CCA) as matrix; negative-ion mode. FAB-MS (*m/z* (%)): *VG-ZAB-2-SEQ* instrument; 3-nitrobenzyl alcohol as matrix. Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH-Zürich.

**1-Benzyl-1,2-dihydro-2-[(trimethylsilyl)ethynyl][60]fullerene (9).** A soln. of **10** (34 mg, 0.040 mmol) in degassed THF (50 ml) was slowly added to excess NaH (50 mg of a 55–65% dispersion in oil, 1.25 mmol), and the resulting mixture was stirred at r.t. for 1 h (TLC: no **10** left). The soln. was transferred under N<sub>2</sub> to a second flask by a cannula mounted with a paper filter. Benzyl bromide was added (50  $\mu$ l, 0.42 mmol), and the mixture was refluxed for 3 h. After addition of toluene (50 ml), the soln. was filtered over a short plug (SiO<sub>2</sub>) and evaporated. Purification by FC (SiO<sub>2</sub>, cyclohexane) and recrystallization (CH<sub>2</sub>Cl<sub>2</sub>/MeOH) gave **9** (17.5 mg, 48%). Brown solid. Spectral data matched with those of samples of **9** prepared before [2c].

**(±)-1,2-Dihydro-1-[(3,4,5,6-tetrahydro-2H-pyran-2-yl)oxymethyl]-2-[(trimethylsilyl)ethynyl][60]fullerene (13).** To **10** (164.5 mg, 0.194 mmol) in degassed THF/Dhp 3:1 (20 ml) was added PPTS (25 mg, 0.1 mmol), and the mixture was refluxed for 2 h. After cooling to r.t. and filtering over a short plug (SiO<sub>2</sub>), the solvent was evaporated. The resulting black residue was dissolved in a small amount of toluene, a 9-fold volume of cyclohexane was added, and the soln. was loaded onto a short plug (SiO<sub>2</sub>). After washing thoroughly with cyclohexane/toluene 9:1 to remove apolar impurities, the product was eluted with cyclohexane/toluene 65:35. Evaporation and recrystallization (CH<sub>2</sub>Cl<sub>2</sub>/MeOH) gave **13** (149 mg, 82.5%). Brown powder. M.p. > 250°. UV/VIS (CH<sub>2</sub>Cl<sub>2</sub>): 697 (300), 432 (3500), 309 (36400), 255 (105500). IR (KBr): 2955m, 2937m, 2866w, 2185w, 2153w, 1248m, 1124m, 1073m, 1036m, 842s, 730s, 526s. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): 5.64 (*d*, *J* = 9.5, 1 H); 5.52 (*d*, *J* = 9.5, 1 H); 5.26 (*br. s*, 1 H); 4.1–3.95 (*m*, 1 H); 3.8–3.7 (*m*, 1 H); 2.0–1.5 (*m*, 6 H); 0.44 (*s*, 9 H). <sup>13</sup>C-NMR (125.77 MHz, CDCl<sub>3</sub>): 153.99; 153.46; 153.18; 153.09; 147.90; 147.75; 147.26; 146.77; 146.58; 146.54; 146.35; 146.30; 146.28; 146.01; 145.99; 145.64; 145.58; 145.57; 145.52; 145.50; 145.45; 145.44; 145.30; 144.84; 144.72; 144.71; 144.65; 143.19; 143.18; 142.72; 142.68; 142.66; 142.31; 142.27; 142.23; 142.13; 142.05; 141.95; 141.92; 141.72; 141.64; 141.49; 141.45; 140.40; 140.31; 139.75; 139.68; 135.42; 135.37; 134.81; 134.17; 103.33; 99.34; 89.84; 74.44; 65.79; 62.14; 58.83; 30.56; 25.56; 19.20; 0.06. MALDI-TOF-MS (ATO): 931.9 (33, *M*<sup>-</sup>), 816.9 (100, [*M* – CH<sub>2</sub>OThp]<sup>-</sup>), 719.5 (5, *C*<sub>60</sub><sup>-</sup>).

**(±)-1-Ethynyl-1,2-dihydro-2-[(3,4,5,6-tetrahydro-2H-pyran-2-yl)oxymethyl][60]fullerene (14).** A soln. of **13** (140 mg, 0.150 mmol) in THF/MeOH 9:1 (150 ml) and K<sub>2</sub>CO<sub>3</sub> (75 mg, 0.54 mmol) was stirred at r.t. until TLC showed the absence of **13**. After filtering over a short plug (SiO<sub>2</sub>) and evaporation, the resulting black residue was dissolved in CS<sub>2</sub> and loaded onto a plug (SiO<sub>2</sub>). The plug was thoroughly rinsed with CS<sub>2</sub> and cyclohexane/toluene 9:1 to remove apolar impurities, whereafter the product was eluted with toluene/cyclohexane 1:1. Evaporation and recrystallization (CS<sub>2</sub>/pentane) gave **14** (115 mg, 89%). Brown powder. M.p. > 250°. UV/VIS (CH<sub>2</sub>Cl<sub>2</sub>): 696 (120), 511 (1070), 431 (3100), 309 (31200), 255 (89900). IR (KBr): 3292w, 2934w, 2863w, 1630w, 1462m, 1429m, 1124s, 1073s, 1033s, 974m, 904m, 767m, 647m, 526s. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): 5.69 (*d*, *J* = 9.4, 1 H); 5.49 (*d*, *J* = 9.4, 1 H); 5.27 (*t*, *J* = 2.8, 1 H); 4.1–4.0 (*m*, 1 H); 3.8–3.7 (*m*, 1 H); 3.00 (*s*, 1 H); 2.0–1.5 (*m*, 6 H). <sup>13</sup>C-NMR (125.77 MHz, CDCl<sub>3</sub>/CS<sub>2</sub> 3:1): 153.59; 152.94; 152.86; 152.80; 147.88; 147.72; 147.10; 146.73; 146.60; 146.58; 146.56; 146.52; 146.33; 146.27; 146.26; 145.93; 145.91; 145.64; 145.61; 145.59; 145.55; 145.52; 145.46; 145.45; 145.42; 145.16; 145.01; 144.80; 144.70; 144.62; 144.59; 143.18; 143.16; 142.71; 142.67; 142.28; 142.23; 142.20; 141.98; 141.92; 141.70; 141.63; 141.46; 141.44; 140.36; 140.28; 139.77; 139.71; 135.28; 135.18; 134.79; 134.30; 99.40; 99.34; 82.68; 74.52; 72.89; 72.85; 65.77; 62.15; 57.49; 30.55; 25.62; 19.21. MALDI-TOF-MS (ATO): 860.1 (63, *M*<sup>-</sup>), 744.6 (100, [*M* – CH<sub>2</sub>OThp]<sup>-</sup>), 719.5 (10, *C*<sub>60</sub><sup>-</sup>). Anal. calc. for C<sub>68</sub>H<sub>12</sub>O<sub>2</sub> (860.84): C 94.88, H 1.41; found: C 94.81, H 1.56.

**2-Ethynyl-1,2-dihydro[60]fullerene-1-methanol (15).** A soln. of **14** (66.5 mg, 0.077 mmol) and PPTS (30 mg, 0.12 mmol) in chlorobenzene/EtOH 10:1 (70 ml) was stirred at 60° for 40 h. Filtration over a short plug (SiO<sub>2</sub>) and

evaporation yielded a black residue which was dissolved in CS<sub>2</sub> and loaded onto a plug (SiO<sub>2</sub>). Rinsing thoroughly with CS<sub>2</sub> followed by elution with toluene gave, after recrystallization (CS<sub>2</sub>/pentane), **15** (57 mg, 95%). Black powder. M.p. > 310°. UV/VIS (CS<sub>2</sub>): 706 (380), 437 (3800). IR (KBr): 3480s (br.), 3285s, 2918m, 2865m, 2186w, 2076w, 1631m, 1509s, 1428s, 1213m, 1180m, 1108m, 1052s, 1043s, 1027s, 768m, 642s, 633s, 552s, 527s. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>/CS<sub>2</sub> 3:1): 5.68 (*d*, *J* = 7.8, 2 H); 3.82 (*t*, *J* = 7.8, 1 H); 3.17 (*s*, 1 H). <sup>13</sup>C-NMR (125.77 MHz, CS<sub>2</sub>/(CD<sub>3</sub>)<sub>2</sub>CO (capillary)): 152.63; 152.08; 147.59; 147.36; 146.35; 146.27; 146.05; 146.00; 145.78; 145.50; 145.48; 145.34; 145.27; 145.21; 144.65; 144.47; 144.30; 142.93; 142.42; 142.40; 141.94; 141.71; 141.68; 141.36; 141.28; 140.03; 139.93; 135.64; 134.56; 83.50; 72.82; 72.14; 69.00; 53.47. MALDI-TOF-MS (DHB): 745.6 (100, [M – CH<sub>2</sub>OH]<sup>+</sup>), 719.5 (28, C<sub>60</sub><sup>-</sup>).

*1,1'-(Buta-1,3-diyne-1,4-diyl)bis[2-(phenylmethyl)[60]fullerene* (**17**). To a vigorously stirred suspension of **12** (30 mg, 0.035 mmol) and CuCl (0.28 g, 2.8 mmol) in PhCl (150 ml) in dry air was added TMEDA (0.4 ml, 2.6 mmol), and the mixture was stirred at r.t. for 24 h. Filtration over a plug (SiO<sub>2</sub>), which was rinsed with PhCl until no more colored material eluted, afforded a soln. which was washed with 5% aq. CuSO<sub>4</sub> soln. (2 × 50 ml), H<sub>2</sub>O (50 ml), and sat. aq. NaCl soln. (50 ml), and dried (Na<sub>2</sub>SO<sub>4</sub>). After evaporation (*T* < 30°), the residue in CS<sub>2</sub> was filtered over a short plug (SiO<sub>2</sub>, CS<sub>2</sub>) and recrystallized from CS<sub>2</sub>/pentane: **17** (15.6 mg, 52%). Brown powder. M.p. > 260°. UV/VIS (PhCl): 698 (700), 435 (9000), 319 (97000). IR (KBr): 3057w, 3023w, 2946m, 2915m, 2863w, 2848w, 2191w, 2131w, 2084w, 1936w, 1740w, 1630w, 1600w, 1494m, 1463m, 1452m, 1431m, 1217w, 1182m, 1029m, 698s, 576m, 552m, 526s. <sup>1</sup>H-NMR (500 MHz, CS<sub>2</sub>/(CD<sub>3</sub>)<sub>2</sub>CO (capillary)): 7.46 (*d*, *J* = 7.1, 4 H); 7.30–7.15 (*m*, 6 H); 5.20 (*s*, 4 H). <sup>13</sup>C-NMR (125.77 MHz, CS<sub>2</sub>/(CD<sub>3</sub>)<sub>2</sub>CO (capillary)): 153.06; 151.80; 147.58; 147.44; 146.39; 146.30; 146.15; 146.04; 146.01; 145.62; 145.53; 145.31; 145.23; 145.20; 144.63; 144.47; 144.36; 142.95; 142.53; 142.50; 142.08; 141.99; 141.71; 141.63; 141.15; 140.24; 138.81; 136.16; 134.42; 134.33; 131.74; 128.19; 127.33; 79.14; 71.65; 66.64; 60.69; 50.92. MALDI-TOF-MS (CCA): 1670.8 (100, M<sup>-</sup>), 1580.5 (38, [M – CH<sub>2</sub>Ph]<sup>-</sup>).

*1,1'-(Buta-1,3-diyne-1,4-diyl)bis[2-(3,4,5,6-tetrahydro-2H-pyran-2-yl)oxymethyl][60]fullerene* (mixture of *meso* form and racemate; **18**). To a vigorously stirred suspension of **14** (75 mg, 0.087 mmol) and CuCl (0.70 g, 7.0 mmol) in PhCl (300 ml) in dry air was added TMEDA (1.0 ml, 6.5 mmol), and the mixture was stirred at r.t. for 17 h. PhCl (250 ml) was added, and the resulting homogeneous soln. was filtered over a short plug (SiO<sub>2</sub>) which was rinsed with toluene/THF 98:2 until no more colored material eluted. The combined eluates were washed with 10% aq. CuSO<sub>4</sub> soln. (3 × 25 ml), H<sub>2</sub>O (50 ml), and sat. aq. NaCl soln. (50 ml) and dried (Na<sub>2</sub>SO<sub>4</sub>). After evaporation (*T* < 30°), the residue in CS<sub>2</sub> was loaded onto a plug (SiO<sub>2</sub>) which was rinsed with CS<sub>2</sub> and then eluted with toluene. Recrystallization from CS<sub>2</sub>/pentane gave **18** (61.5 mg, 82%). Brown solid. M.p. > 310°. UV/VIS (CS<sub>2</sub>): 704 (870), 636 (1000), 437 (9000). IR (KBr): 2934m, 2916m, 2862m, 2845m, 1631w, 1462m, 1430m, 1182m, 1125s, 1074s, 1035s, 974m, 904m, 768m, 552m, 526s. <sup>1</sup>H-NMR (500 MHz, CS<sub>2</sub>/(CD<sub>3</sub>)<sub>2</sub>CO (capillary)): 5.65 (*d*, *J* = 9.3, 2 H); 5.43 (2*d*, *J* = 9.3, 2 H); 5.30–5.25 (*m*, 2 H); 4.1–4.0 (*m*, 2 H); 3.70–3.65 (*m*, 2 H); 2.05–1.55 (*m*, 12 H). <sup>13</sup>C-NMR (125.77 MHz, CS<sub>2</sub>/(CD<sub>3</sub>)<sub>2</sub>CO (capillary)): 153.07; 152.30; 151.38; 151.35; 147.60; 147.43; 146.46; 146.38; 146.36; 146.32; 146.29; 146.12; 146.08; 146.03; 145.57; 145.54; 145.52; 145.49; 145.42; 145.33; 145.29; 145.22; 145.18; 144.75; 144.67; 144.55; 144.46; 144.35 (2 ×); 142.97; 142.94; 142.51; 142.47; 142.04; 142.01; 141.98; 141.77; 141.73; 141.71; 141.50; 141.44; 141.26; 140.22; 140.15; 139.75; 139.70; 135.17; 135.07; 134.76; 134.34; 99.07; 78.79; 74.60; 69.02; 66.45; 61.69; 57.96; 30.67; 26.07; 19.60. MALDI-TOF-MS (ATO): 1718.0 (36, M<sup>-</sup>), 1602.7 (36, [M – CH<sub>2</sub>OThp]<sup>-</sup>), 896.5 (18, [M – C<sub>60</sub> – OThp]<sup>-</sup>), 768.0 (23, [M – C<sub>60</sub>CH<sub>2</sub>OThp – CH<sub>2</sub>OThp]<sup>-</sup>), 744.4 (17, [M – 2 CH<sub>2</sub>OThp]<sup>2-</sup>), 719.2 (100, C<sub>60</sub><sup>-</sup>).

*1,1'-(Buta-1,3-diyne-1,4-diyl)bis[60]fullerene-2-methanol* (**19**). A soln. of **18** (25 mg, 0.015 mmol) and PPTS (100 mg, 0.4 mmol) in chlorobenzene/EtOH 10:1 (275 ml) was stirred at 60° for 65 h. Washing with H<sub>2</sub>O (2 × 50 ml) and sat. aq. NaCl soln. (50 ml), drying (Na<sub>2</sub>SO<sub>4</sub>), and evaporation (*T* < 30°) to a volume of 5 ml yielded **19** (18 mg, 80%). Shiny black crystals. M.p. > 260°. UV/VIS (1,2-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub>): 699 (2900), 434 (14000), 318 (94000). IR (KBr): 3350s (br.), 2918w, 2865w, 1636w, 1461w, 1421m, 1213w, 1180m, 1112w, 1042s, 765m, 692m, 574m, 551m, 526s. MALDI-TOF-MS (CCA): 1550.8 (100, M<sup>-</sup>), 1518.8 (14, [M – H – CH<sub>2</sub>OH]<sup>-</sup>), 778.6 (80).

(±)-*1-[3,4,5,6-Tetrahydro-2H-pyran-2-yl]oxymethyl-2-[4-(trimethylsilyl)buta-1,3-diyne-1-yl][60]fullerene* (**20**). To a vigorously stirred suspension of **14** (80 mg, 0.093 mmol), Me<sub>3</sub>SiC≡CH (0.73 ml, 5.2 mmol), and CuCl (2.70 g, 27.3 mmol) in PhCl (500 ml) in dry air was added TMEDA (4.0 ml, 26.6 mmol), and the mixture was stirred at r.t. for 30 min until complete disappearance of **14** (TLC). The soln. was filtered over a short plug (SiO<sub>2</sub>) which was rinsed with PhCl until no more colored material eluted. Washing with 5% aq. CuSO<sub>4</sub> soln. (3 × 30 ml), H<sub>2</sub>O (50 ml), and sat. aq. NaCl soln. (50 ml) and drying (Na<sub>2</sub>SO<sub>4</sub>), followed by evaporation (*T* < 30°), yielded a residue which was dissolved in CS<sub>2</sub> and loaded onto a plug (SiO<sub>2</sub>). Rinsing the plug with CS<sub>2</sub> and eluting with toluene/cyclohexane 1:1, evaporation (*T* < 30°), and recrystallization (CS<sub>2</sub>/pentane) gave **20** (45.5 mg, 51%). Black crystals. M.p. > 260°. UV/VIS (CH<sub>2</sub>Cl<sub>2</sub>): 695 (300), 432 (3600), 312 (41 500), 256 (121 700). IR (KBr): 2935m, 2918m, 2862m, 2845m, 2214w, 2089m, 1630w, 1428m, 1248m, 1125m, 1075m, 1036m, 843s, 759m, 526s. <sup>1</sup>H-NMR

(200 MHz, CDCl<sub>3</sub>): 5.64 (*d*, *J* = 9.5, 1 H); 5.45 (*d*, *J* = 9.5, 1 H); 5.33 (br. *s*, 1 H); 4.2–4.0 (*m*, 1 H); 3.8–3.7 (*m*, 1 H); 2.05–1.6 (*m*, 6 H); 0.31 (*s*, 9 H). <sup>13</sup>C-NMR (125.77 MHz, CDCl<sub>3</sub>): 153.45; 152.45; 151.90; 151.85; 147.89; 147.74; 146.63; 146.61; 146.59; 146.58; 146.53; 146.34; 146.32; 146.28; 146.20; 145.87; 145.83; 145.65; 145.62; 145.59; 145.54; 145.49; 145.44; 145.13; 145.00; 144.79; 144.66; 144.61; 144.59; 143.16; 143.13; 142.71; 142.66; 142.25; 142.23; 142.19; 142.01; 141.95; 141.93; 141.90; 141.67; 141.59; 141.47; 141.44; 140.34; 140.26; 139.93; 139.86; 135.56; 135.43; 135.00; 134.44; 99.94; 88.20; 87.78; 76.85; 75.30; 68.89; 66.91; 62.45; 58.07; 30.53; 25.56; 19.33; –0.39. MALDI-TOF-MS (DHB): 955.6 (10, *M*<sup>+</sup>), 840.9 (100, [*M* – CH<sub>2</sub>OThp]<sup>+</sup>), 719.5 (65, C<sub>60</sub><sup>-</sup>). Anal. calc. for C<sub>73</sub>H<sub>20</sub>O<sub>2</sub>Si (957.05): C 91.62, H 2.11; found: C 91.37, H 2.27.

2-[4-(Trimethylsilyl)buta-1,3-dien-1-yl][60]fullerene-1-methanol (**21**). A soln. of **20** (25 mg, 0.026 mmol) and PPTS (25 mg, 0.1 mmol) in CHCl<sub>3</sub>/EtOH 9:1 (100 ml) was stirred at 60° for 72 h, then filtered over a short plug (SiO<sub>2</sub>) and evaporated. The resulting brown residue was dissolved in CS<sub>2</sub> and loaded onto a plug (SiO<sub>2</sub>) which was rinsed with CS<sub>2</sub> and eluted with toluene/cyclohexane 1:1. Evaporation and recrystallization from CS<sub>2</sub>/pentane gave **21** (19.5 mg, 86%). Black crystals. M.p. > 250°. UV/VIS (CH<sub>2</sub>Cl<sub>2</sub>): 695 (350), 432 (3700), 313 (42000), 255 (124000). IR (KBr): 3350s (br.), 2946m, 2919m, 2863w, 2210w, 2198w, 2083w, 1630w, 1425m, 1247m, 1052m, 1042m, 886m, 842s, 758m, 526s. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): 5.68 (*d*, *J* = 7.3, 2 H); 3.58 (*t*, *J* = 7.3, 1 H); 0.32 (*s*, 9 H). <sup>13</sup>C-NMR (125.77 MHz, CS<sub>2</sub>/(CD<sub>3</sub>)<sub>2</sub>CO (capillary)): 152.31; 151.17; 147.59; 147.39; 146.36; 146.30; 146.07; 146.02; 145.78; 145.49; 145.47; 145.37; 145.30; 145.22; 144.57; 144.47; 144.31; 142.91; 142.44; 142.41; 141.96; 141.76; 141.67; 141.41; 141.29; 140.05; 139.99; 135.68; 134.62; 89.31; 87.68; 76.20; 71.91; 70.14; 69.23; 53.47; –0.48. MALDI-TOF-MS (DHB): 872.2 (10, *M*<sup>+</sup>), 841.2 (75, [*M* – CH<sub>2</sub>OH]<sup>+</sup>), 719.8 (100, C<sub>60</sub><sup>-</sup>).

61-[3-(Trimethylsilyl)prop-2-ynylidene]-1,2-(methoxymethano)[60]fullerene (**24**). To a soln. of **21** (14 mg, 16 μmol) in THF (10 ml), which had been carefully degassed, was added at 0° 3 ml (20 μmol) of a soln. of DBU (10 μl) in THF (10 ml), and the mixture was stirred at r.t. for 10 h. After evaporation, the residue was dissolved in CS<sub>2</sub> and purified by FC (SiO<sub>2</sub>): **24** (6.8 mg, 49%). R<sub>f</sub> 0.3 (cyclohexane). <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): 6.02 (*s*, 2 H); 5.85 (*s*, 1 H); 0.32 (*s*, 9 H). <sup>13</sup>C-NMR (125.77 MHz, CS<sub>2</sub>/(CD<sub>3</sub>)<sub>2</sub>CO (capillary)): 166.05 (C(61)–O); 151.69; 151.48; 147.22; 147.16; 146.16; 146.11; 145.92; 145.60; 145.47; 145.43; 145.30; 145.17; 145.11; 144.35; 144.31; 143.04; 142.64; 142.20; 142.03; 142.00; 141.97; 140.72; 140.28; 135.80; 134.73 (25 fullerene sp<sup>2</sup>-C-atom resonances out of 30 expected); 100.10; 85.96; 81.94; 76.74; 69.21; –0.38. MALDI-TOF-MS (DHB): 872.3 (5, *M*<sup>+</sup>), 733 (100, [C<sub>61</sub>H<sub>2</sub>]<sup>+</sup>), 718.9 (100, C<sub>60</sub><sup>-</sup>).

Decaethyl 66,66-Bis[(trimethylsilyl)ethynyl]-1,2:18,36:22,23:27,45:31,32:55,56-hexakis(methano)[60]fullerene-61,61,62,62,63,63,64,64,65,65-decarboxylate (**26**). A soln. of **25** (145 mg, 0.156 mmol) [2c] and DMA (323 mg, 1.56 mmol) in dry toluene (14.5 ml) was degassed and subsequently stirred at r.t. for 2 h. Diethyl 2-bromomalonate (210 μl, 1.24 mmol) and DBU (280 μl, 1.87 mmol) were successively added, and the dark red soln. was stirred for 5 d at r.t., then diluted with CH<sub>2</sub>Cl<sub>2</sub> (100 ml), washed with H<sub>2</sub>O (3 × 10 ml), and dried (MgSO<sub>4</sub>). Evaporation of the solvent, FC (2 × ; SiO<sub>2</sub>, cyclohexane/AcOEt 7:3, then SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane 4:1) gave **26** (75 mg, 28%). Yellow solid. M.p. > 240°. UV/VIS (CH<sub>2</sub>Cl<sub>2</sub>): 336 (46300), 316 (55500), 281 (87600), 273 (sh 84600), 244 (106000). IR (CHCl<sub>3</sub>): 3028w, 2985w, 2970w, 2939w, 2172w, 1740s, 1601w, 1465w, 1368m, 1298m, 1265s, 1250s, 1095w, 1080w, 1038w, 1016m, 848s. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): 4.39–4.27 (*m*, 20 H); 1.33 (3*t*, *J* = 7.1, 18 H); 1.30 (*t*, *J* = 7.1, 12 H); 0.18 (*s*, 18 H). <sup>13</sup>C-NMR (125.77 MHz, CDCl<sub>3</sub>): 163.84; 163.82; 163.79; 163.77; 145.96; 145.87; 145.76; 145.70; 141.62; 141.49; 141.13; 141.06; 141.02; 97.59; 89.48; 73.21; 69.20; 69.15; 69.13; 68.90; 63.83; 62.77; 45.36; 45.23; 44.78; 21.34; 14.03; 14.00; –0.11. FAB-MS: 1718.3 (14, [<sup>13</sup>C<sup>12</sup>C<sub>105</sub>H<sub>68</sub>O<sub>20</sub>Si<sub>2</sub> + H]<sup>+</sup>), 1672.3 (8, [*M* – OEt]<sup>+</sup>), 1511.0 (44, [*M* – C(C≡CSiMe<sub>3</sub>)<sub>2</sub>]<sup>+</sup>), 1465.6 (6, [*M* – C(C≡CSiMe<sub>3</sub>)<sub>2</sub> – OEt]<sup>+</sup>), 1352.5 (31, [*M* – C(C≡CSiMe<sub>3</sub>)<sub>2</sub> – C(CO<sub>2</sub>Et)<sub>2</sub>]<sup>+</sup>), 1194.4 (17, [*M* – C(C≡CSiMe<sub>3</sub>)<sub>2</sub> – 2 C(CO<sub>2</sub>Et)<sub>2</sub>]<sup>+</sup>), 1036.4 (14, [*M* – C(C≡CSiMe<sub>3</sub>)<sub>2</sub> – 3 C(CO<sub>2</sub>Et)<sub>2</sub>]<sup>+</sup>), 878.1 (11, [*M* – C(C≡CSiMe<sub>3</sub>)<sub>2</sub> – 4 C(CO<sub>2</sub>Et)<sub>2</sub>]<sup>+</sup>), 720.0 (100, C<sub>60</sub><sup>+</sup>). Anal. calc. for C<sub>106</sub>H<sub>68</sub>O<sub>20</sub>Si<sub>2</sub> (1717.8): C 74.11, H 3.99; found: C 73.86, H 3.51.

Decaethyl 66,66-Diethynyl-1,2:18,36:22,23:27,45:31,32:55,56-hexakis(methano)[60]fullerene-61,61,62,62,63,63,64,64,65,65-decarboxylate (**27**). To a soln. of **26** (45 mg, 0.026 mmol) in wet THF (15 ml) was added Bu<sub>4</sub>NF adsorbed (1.1 mmol/g) on SiO<sub>2</sub> (60 mg, 0.066 mmol), and the suspension was stirred at r.t. for 1 h, then poured into sat. aq. NH<sub>4</sub>Cl soln./toluene (30 ml). Washing with H<sub>2</sub>O (3 × 10 ml), drying (MgSO<sub>4</sub>), and evaporation *in vacuo* gave a residue which was dissolved in a small amount of CH<sub>2</sub>Cl<sub>2</sub> and filtered over a short plug (SiO<sub>2</sub>). Evaporation gave **27** (35 mg, 85%). Yellow solid. M.p. > 240°. UV/VIS (CH<sub>2</sub>Cl<sub>2</sub>): 335 (49600), 316 (58400), 281 (91500), 272 (86400), 244 (111100). IR (CHCl<sub>3</sub>): 3303m, 3028w, 2123w, 1739s, 1601w, 1465w, 1368m, 1298m, 1264s, 1095w, 1014m, 848s. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): 4.32 (*q*, *J* = 7.1, 12 H); 4.31 (*q*, *J* = 7.1, 4 H); 4.30 (*q*, *J* = 7.1, 4 H); 2.54 (*s*, 2 H); 1.31 (3*t*, *J* = 7.1, 24 H); 1.30 (*t*, *J* = 7.1, 6 H). <sup>13</sup>C-NMR (125.77 MHz, CDCl<sub>3</sub>): 163.79; 163.74; 163.69; 145.99; 145.97; 145.80; 145.76; 145.71; 145.65; 141.56; 141.24; 141.14; 141.12; 141.10; 141.04; 76.61; 72.49; 71.80; 69.20; 68.95; 62.90; 62.85; 45.45; 45.32; 44.84; 19.15; 14.05; 14.02. FAB-MS: 1572.9 (45, *M*<sup>+</sup>),

1527.8 (23,  $[M - OEt]^+$ ), 1510.6 (19,  $[M - C(C\equiv CH)_2]^+$ ), 1414.8 (44,  $[M - C(CO_2Et)_2]^+$ ), 1369.5 (13,  $[M - C(CO_2Et)_2 - OEt]^+$ ), 1352.4 (43,  $[M - C(C\equiv CH)_2 - C(CO_2Et)_2]^+$ ), 1194.4 (14,  $[M - C(C\equiv CH)_2 - 2 C(CO_2Et)_2]^+$ ), 1035.8 (9,  $[M - C(C\equiv CH)_2 - 3 C(CO_2Et)_2]^+$ ), 719.8 (100,  $C_{60}^+$ ).

*Decaethyl 55,56-Dihydro-55-(3,4,5,6-tetrahydro-2H-pyran-2-yl)oxymethyl]-56-(trimethylsilyl)ethynyl]-1,2:18,36:22,23:27,45:31,32-pentakis(methano)[60]fullerene-61,61,62,62,63,63,64,64,65,65-decarboxylate (28)*. A soln. of **13** (115 mg, 0.123 mmol) and DMA (255 mg, 1.23 mmol) in dry toluene (12 ml) was degassed and stirred at r.t. for 3 h. Diethyl 2-bromomalonate (166  $\mu$ l, 0.986 mmol) and DBU (147  $\mu$ l, 0.986 mmol) were successively added, and the dark red soln. was stirred for 5 d at r.t., then diluted with toluene (100 ml), washed with  $H_2O$  ( $3 \times 10$  ml), dried ( $Na_2SO_4$ ), and filtered through a short plug ( $SiO_2$ ) which was thoroughly rinsed with toluene to remove DMA and subsequently with AcOEt until no more colored material eluted. The red AcOEt fraction was evaporated and the residue purified by FC ( $SiO_2$  *H*, cyclohexane/AcOEt 7:3) to give 62 mg of an orange solid which was recrystallized (AcOEt/cyclohexane) to provide **28** (46.5 mg, 22%). Yellow solid. M.p. > 255°. UV/VIS ( $CH_2Cl_2$ ): 330 (sh, 37 700), 309 (sh, 55 400), 286 (63 000), 269 (64 300), 240 (78 300). IR (KBr): 2979m, 2927m, 2848m, 2156w, 1745s, 1464m, 1446m, 1391m, 1368m, 1295m, 1265s, 1218s, 1123m, 1079m, 1021m, 907w, 856m, 759m, 713m, 530m.  $^1H$ -NMR (500 MHz,  $CDCl_3$ ): 4.89 (br. s, 1 H); 4.84 (d,  $J = 9.6$ , 1 H); 4.74 (d,  $J = 9.6$ , 1 H); 4.39 (q,  $J = 7.1$ , 4 H); 4.35–4.25 (m, 14 H); 4.23 (q,  $J = 7.1$ , 2 H); 3.85–3.75 (m, 1 H); 3.60–3.50 (m, 1 H); 1.95–1.40 (m, 6 H); 1.37 (t,  $J = 7.1$ , 6 H); 1.35–1.25 (m, 24 H); 0.22 (s, 9 H).  $^{13}C$ -NMR (125.77 MHz,  $CDCl_3$ ): 164.14; 164.09; 163.98; 163.93; 163.71; 163.66; 163.62; 163.44; 152.28; 151.68; 151.30; 151.27; 146.76; 146.47; 146.33; 146.22; 146.16; 146.06; 145.77; 145.73; 145.64; 145.62; 145.46; 145.45; 145.44; 145.42; 145.30; 145.28; 145.21; 145.18; 144.84; 144.42; 143.00; 142.99; 142.60; 142.17; 142.09; 141.98; 141.86; 141.71; 141.69; 141.68; 139.81; 139.77; 139.63; 139.53; 139.21; 139.07; 138.82; 138.72; 138.67; 138.65; 103.16; 99.06; 88.36; 74.42; 70.03; 69.65; 69.54; 69.18; 69.14; 67.45; 67.41; 67.27; 67.20; 62.86; 62.83; 62.74; 62.72; 62.66; 62.42; 62.37; 61.59; 55.78; 45.36; 45.06; 44.79; 40.43; 30.17; 25.49; 18.89; 14.05; 14.04; 14.01; 13.98; –0.14. FAB-MS: 1724.9 (21,  $[^{13}C^{12}C_{105}H_{70}O_{22}Si + H]^+$ ), 1679.4 (25,  $[M + H - OEt]^+$ ), 1622.6 (85,  $[M - OThp]^+$ ), 1609.4 (40,  $[M + H - CH_2OThp]^+$ ), 1562.6 (30,  $[M + H - C(CO_2Et)_2]^+$ ), 1512.0 (44,  $[M + H - CH_2OThp - C\equiv CSiMe_3]^+$ ), 1466.0 (33,  $[M + H - CH_2OThp - C\equiv CSiMe_3 - OEt]^+$ ), 1352.4 (16,  $[M - CH_2OThp - C\equiv CSiMe_3 - C(CO_2Et)_2]^+$ ), 1194.6 (20,  $[M - CH_2OThp - C\equiv CSiMe_3 - 2 C(CO_2Et)_2]^+$ ), 1036.3 (35,  $[M - CH_2OThp - C\equiv CSiMe_3 - 3 C(CO_2Et)_2]^+$ ), 878.1 (20,  $[M - CH_2OThp - C\equiv CSiMe_3 - 4 C(CO_2Et)_2]^+$ ), 720.1 (100,  $C_{60}^+$ ). Anal. calc. for  $C_{106}H_{70}O_{22}Si$  (1723.79): C 73.86, H 4.09; found: C 73.37, H 4.57.

*Decaethyl 55,56-Dihydro-55-(hydroxymethyl)-56-(trimethylsilyl)ethynyl]-1,2:18,36:22,23:27,45:31,32-pentakis(methano)[60]fullerene-61,61,62,62,63,63,64,64,65,65-decarboxylate (29)*. A suspension of **28** (39 mg, 0.023 mmol) and PPTS (20 mg, 0.080 mmol) in EtOH (10 ml) was heated at 60° for 2 h, whereafter the soln. had become clear. Stirring at r.t. overnight, diluting with  $CH_2Cl_2$  (50 ml), filtering over a short plug ( $SiO_2$ ), and evaporation gave a yellow-orange solid, which was recrystallized (AcOEt/cyclohexane): **29** (31.5 mg, 85%). Yellow solid. M.p. > 260°. UV/VIS ( $CH_2Cl_2$ ): 329 (sh, 31 700), 308 (sh, 46 300), 285 (52 600), 269 (53 400), 239 (sh, 66 800). IR (KBr): 3551m, 2979m, 2929m, 2849w, 2155w, 1745s, 1464m, 1446m, 1391m, 1368m, 1296m, 1258s, 1218s, 1120m, 1082m, 1021m, 856m, 761m, 713m, 531m.  $^1H$ -NMR (300 MHz,  $CDCl_3$ ): 4.87 (d,  $J = 7.2$ , 2 H); 4.39 (q,  $J = 7.1$ , 4 H); 4.4–4.2 (m, 16 H); 3.71 (t,  $J = 7.2$ , 1 H); 1.37 (t,  $J = 7.1$ , 6 H); 1.35–1.25 (m, 24 H); 0.27 (s, 9 H).  $^{13}C$ -NMR (125.77 MHz,  $CDCl_3$ ): 164.07; 164.03; 163.87; 163.83; 163.69; 163.53; 163.46; 151.68; 150.84; 146.24; 146.16; 145.91; 145.76; 145.47; 145.46; 145.44; 145.24; 145.11; 144.61; 143.73; 142.45; 142.17; 142.11; 141.73; 141.69; 139.90; 139.82; 139.59; 139.48; 139.18; 139.06; 104.14; 89.19; 73.04; 70.02; 69.67; 69.61; 69.16; 67.49; 67.48; 66.62; 62.89; 62.86; 62.80; 62.75; 62.74; 62.68; 54.79; 45.48; 45.19; 45.01; 40.51; 14.04; 13.99; –0.25. FAB-MS: 1639.0 (100,  $[^{13}C^{12}C_{100}H_{62}O_{21}Si]^+$ ), 1622.3 (24,  $[M - OH]^+$ ), 1609.3 (10,  $[M - CH_2OH]^+$ ), 1593.5 (75,  $[M - OEt]^+$ ), 1562.6 (30,  $[M - CH_2OH - OEt]^+$ ), 1510.8 (9,  $[M - CH_2OH - C\equiv CSiMe_3]^+$ ), 1465.3 (9,  $[M - CH_2OH - C\equiv CSiMe_3 - OEt]^+$ ), 1352.3 (6,  $[M - CH_2OH - C\equiv CSiMe_3 - C(CO_2Et)_2]^+$ ), 1194.6 (6,  $[M - CH_2OH - C\equiv CSiMe_3 - 2 C(CO_2Et)_2]^+$ ), 1036.6 (4,  $[M - CH_2OH - C\equiv CSiMe_3 - 3 C(CO_2Et)_2]^+$ ), 878.5 (4,  $[M - CH_2OH - C\equiv CSiMe_3 - 4 C(CO_2Et)_2]^+$ ), 720.0 (26,  $C_{60}^+$ ). Anal. calc. for  $C_{101}H_{62}O_{21}Si$  (1639.6): C 73.98, H 3.81; found: C 73.52, H 3.88.

*Decaethyl 55,56-Dihydro-55-(trimethylsilyl)ethynyl]-1,2:18,36:22,23:27,45:31,32-pentakis(methano)[60]fullerene-61,61,62,62,63,63,64,64,65,65-decarboxylate (30)*. A soln. of **29** (34.5 mg, 0.021 mmol) in THF/EtOH 7:1 (40 ml) was cooled to 0°, and  $K_2CO_3$  (50 mg, 0.36 mmol) was added. After stirring at 0° for 9 h ( $^1H$ -NMR: no **29** left), the mixture was filtered over a short plug ( $SiO_2$ ) and evaporated. The resulting brown residue in  $CH_2Cl_2$  was filtered over a short plug ( $SiO_2$ ), and evaporation gave a red-orange residue (17.5 mg, 53%), which was 6:4 mixture of **30** and all-*e*  $C_{2v}$  pentaadduct  $C_{60}(C(CO_2Et)_2)_5$  [17a]. **30**:  $^1H$ -NMR (200 MHz,  $CDCl_3$ ): 5.71 (s, 1 H); 4.5–4.2 (m, 20 H); 1.45–1.2 (m, 30 H); 0.25 (s, 9 H). FAB-MS: 1609.4 (100,  $[^{13}C^{12}C_{99}H_{60}O_{20}Si]^+$ ), 1563.7 (24,  $[M - OEt]^+$ ), 1510.6 (7,  $[M - H - C\equiv CSiMe_3]^+$ ), 1465.5 (4,  $[M - H - C\equiv CSiMe_3 - OEt]^+$ ), 1194.4

(3,  $[M - H - C \equiv CSiMe_3 - 2 C(CO_2Et)_2]^+$ ), 1036.3 (5,  $[M - H - C \equiv CSiMe_3 - 3 C(CO_2Et)_2]^+$ ), 878.2 (7,  $[M - H - C \equiv CSiMe_3 - 4 C(CO_2Et)_2]^+$ ), 720.2 (39,  $C_{60}^+$ ).

*Electrochemical Measurements.* The electrochemical studies were carried out in  $PhCl/CH_2Cl_2$  1:1. The supporting electrolyte was  $(Bu_4N)PF_6$  (0.1M). All measurements were carried out using a classical three-electrode cell. The working electrode was a glassy C-electrode (diameter 2 mm), the auxiliary electrode a Pt-wire, and the reference electrode a Ag-wire (pseudo-reference electrode). All potentials in the text are given vs.  $Fc/Fc^+$  used as internal standard. The cell was connected to a computerized multipurpose electrochemical device DACFAMOV (Microtec CNRS, Toulouse, France) connected to an *Apple II* microcomputer.

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