Pergamon

Tetrahedron, Vol. 52, No. 14, pp. 4925-4947, 1996

0040-4020/96 $15.00 + 0.00

S0040-4020(96)00102-0

Fullerene-Acetylene Hybrids: Towards a Novel Class of Molecular Carbon Allotropes

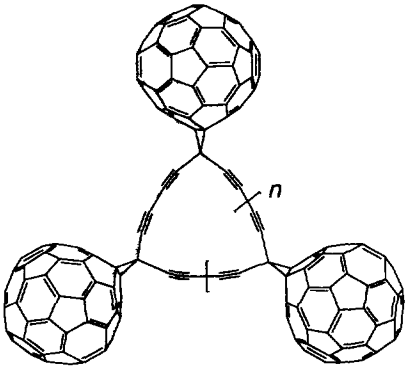
Peter Timmerman, Harry L. Anderson, Rüdiger Faust, Jean-François Nierengarten, Tilo Habicher, Paul Seiler, François Diederich*

Laboratorium für Organische Chemie, ETH-Zentrum, Universitätstrasse 16,
CH-8092 Zürich (Switzerland)

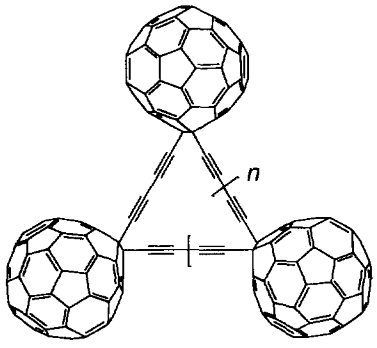
Abstract: *The synthesis and complete characterization of 17 new fullerene-acetylene covalent derivatives is described. Reaction of 3-bromo-1,5-bis(trimethylsilyl)penta-1,4-diyne (5) with C_{60} gave bis-protected diethynylmethanofullerene **4** in 56% yield. Unsymmetrically bis-protected diethynylmethanofullerene **6** was synthesized in 53% yield from tosylhydrazone **7** and C_{60}. Proto-desilylation of **4** and **6** gave the corresponding free alkynes **3** and **8** in 83% and 69% yield, respectively. Partial deprotection of **4** afforded mono-protected fullerene **9** in 35% yield. Oxidative hetero-coupling reactions of **3** and **8** under Hay conditions with various monosubstituted acetylenes gave the butadiynylmethanofullerenes **10-13** in yields varying from 25-49%. Homo-coupling of **8** produced dumbbell-shaped fullerene **14**, the first dimeric fullerene that could be fully characterized. The X-ray crystal structure analysis of **14** revealed little or no electronic interaction between the two fullerene spheres. Addition of lithium trimethylsilylacetylide to C_{60} gave access to 1-substituted-2-(trimethylsilylethynyl)fullerenes. The acidity of hydrofullerene **16**, synthesized in 58% yield, was studied as a function of base and solvent. Reaction of lithiated fullerene **17** with various electrophiles is discussed. Alcohol **25** was prepared in 57% yield by reaction of **17** with formaldehyde. Under strongly basic conditions, **25** eliminates formaldehyde to give **16** in quantitative yield. Oxidation of **25** afforded aldehyde **27** in 53% yield, a rather unstable compound that is easily converted to hydrofullerene **16**. Conversion of **25** to the corresponding tosylate could be performed in 40% yield.*

1. INTRODUCTION

In light of our ongoing interest in synthetic carbon-rich materials,[1] we recently started a research program on the synthesis of molecular carbon allotropes based on a combination of fullerenes and acetylenes.[2] The general idea is to utilize the steric shielding of end-capping C_{60}-spheres to stabilize a central acetylenic framework. As a start, we focused our attention on two different types of macrocyclic polyynes, **1** and **2**, in which the fullerenes are either attached to the acetylenic core via methano bridges, or are incorporated into the macrocycle itself. In comparison with related acetylenic macrocycles that had been reported previously,[1,3] the use of fullerene "end-caps", as in **1** and **2**, avoids the incorporation of any elements other than carbon, leading to a new family of carbon allotropes. Moreover, electronic communication between the fullerene and acetylenic substructures, either by through-bond or by through-space orbital interactions,[4] could largely extend the conjugation pathway within the framework, thereby leading to interesting physical properties.



1



2

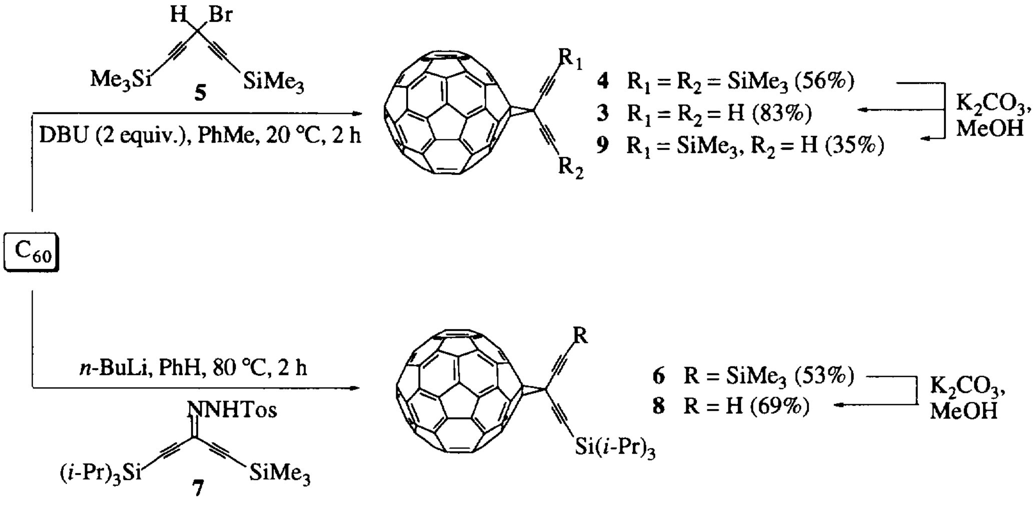
In this paper we describe 17 new fullerene-acetylene derivatives that were prepared in connection with the development of the carbon allotropes **1** and **2**. Their synthesis and characterization together with some of their interesting chemical and spectroscopic properties will be discussed in detail. Some of the compounds exhibit quite unusual chemical reactivity, which gives new insight to and creates new perspectives in fullerene chemistry.

2. RESULTS AND DISCUSSION

2.1. *Bis(alkynyl)methanofullerenes[60]*

2.1.1. Synthesis. An attractive and convenient route for the synthesis of the fullerene-acetylene hybrid allotropes **1** (n = 1-3) relies on the oxidative coupling of diethynylmethanofullerene **3** (*Scheme 1*). Rubin and co-workers[5] recently prepared bis(trimethylsilylethynyl)methanofullerene **4** by reacting C_{60} with the carbene derived from the tosylhydrazone of 1,5-bis(trimethylsilyl)penta-1,4-diyn-3-one under Bamford-Stevens reaction conditions. We found that reaction of 3-bromo-1,5-bis(trimethylsilyl)penta-1,4-diyne (**5**)[6] with C_{60} in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene gave **4** after 2 h in 56% yield (*Scheme 1*), analogously to the cyclopropanation of C_{60} with α-halocarbonyl compounds reported by Bingel.[7] In this reaction, DBU can simply act as a base (pK_a = 24.3 in MeCN) for the deprotonation of **5** or, more likely, can react with **5** as a nucleophile to give a more acidic onium salt[8] that, after deprotonation to the corresponding nitrogen ylide, attacks C_{60}. Purification of **4** was easily performed by a simple recrystallization from cyclohexane followed by redissolving the crystals in THF and filtering from unreacted C_{60} over Celite. The Bamford-Stevens reaction was applied to obtain the unsymmetrically protected derivative **6**. Tosylhydrazone **7** was treated with n-BuLi in benzene at room temperature followed by thermolysis of the resulting lithium salt in refluxing benzene, which generates the corresponding carbene that reacts with C_{60}. In this way, compound **6** was obtained in 53% yield after flash chromatography and recrystallization.

The trialkylsilyl protecting groups in **4** and **6** greatly enhance the solubility of these C_{60} derivatives in common organic solvents (THF, hexane, aromatic hydrocarbons, CH_2Cl_2, $CHCl_3$), which facilitated their spectroscopic characterization. Both cyclopropanations occur at the 6-6 ring junction leading to structures with closed transannular bonds (6-6 closed).[9] In the ^{13}C NMR spectra all 17 fullerene resonances expected for **4** (C_{2v} symmetry) are well resolved while 29 out of the 32 fullerene resonances were clearly discernible for **6** with C_s symmetry. Diagnostic for both compounds are the resonances of the methano bridge C atoms at $\delta = 27.47$ (**4**) and $\delta = 32.24$ (**6**), along with the respective bridgehead carbon resonances at $\delta = 75.60$ (**4**) and $\delta = 75.58$ (**6**).



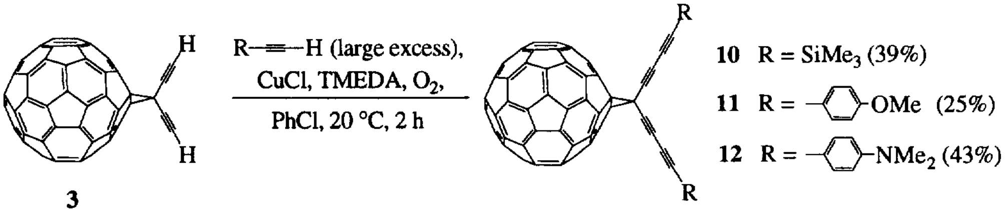
Scheme 1. Synthesis and proto-desilylation of trimethylsilyl-protected diethynylmethanofullerenes.

Proto-desilylation of **4** and **6** was effected by K_2CO_3 in THF/MeOH to give the parent hydrocarbon **3** and regioselectively deprotected **8** in 83% and 69% yield, respectively. The ^1H NMR signals of the acetylenic protons appeared at $\delta = 2.87$ (**3**, in $CS_2/CDCl_3$ 1:1) and $\delta = 2.88$ (**8**, in $CDCl_3$). Full deprotection of **4** took approx. 2 h at room temperature and could be easily followed by TLC (SiO_2, hexane). When the reaction was quenched after approx. 90 min with acetic acid, a mixture of three compounds, *i. e.* starting material, hydrocarbon **3**, and mono-deprotected **9**, was obtained. From this mixture **9** was isolated in 35% yield after flash chromatography and recrystallization. Mono-deprotected **9** is of particular interest for the sequential built-up of fullerene-acetylene hybrid structures of type **1** since its Me_3Si protecting group can be removed under much milder conditions than the $(i\text{-Pr})_3Si$ group in mono-deprotected **8**.

2.1.2. Oxidative Coupling Reactions. In order to probe the potential of diethynylmethanofullerenes as building blocks for molecular carbon allotropes, **3** was subjected to Hay coupling conditions. However, attempts to cyclooligomerize **3** did not yield tractable products, mainly due to their expected poor solubility.

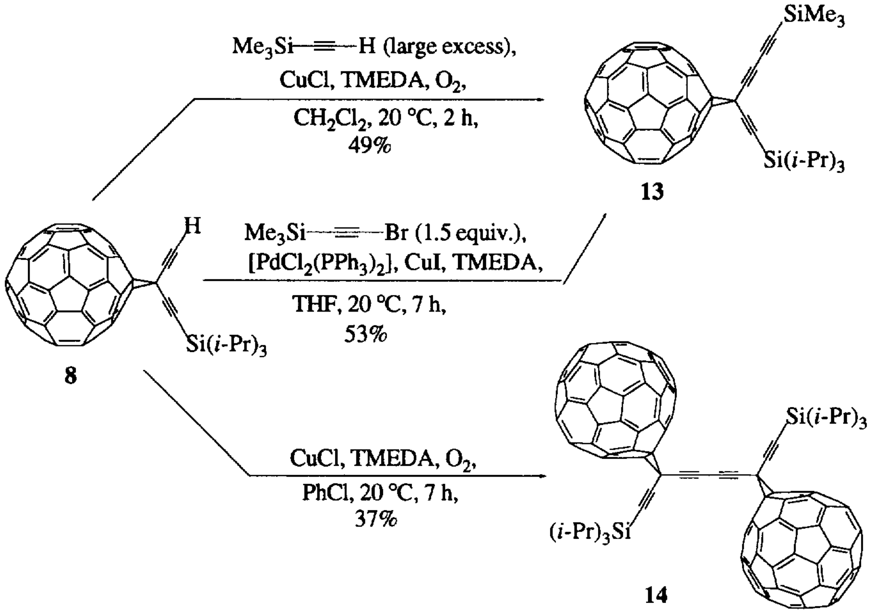
This prompted us to investigate hetero-coupling reactions between **3** and various monosubstituted acetylene derivatives under conditions previously developed for the preparation of butadiynyl porphyrins.[10]

In situ preparation of the Hay catalyst (CuCl, *N,N,N',N'*-tetramethylethylenediamine (TMEDA), dry air) in chlorobenzene in the presence of **3** and a large excess of trimethylsilylacetylene indeed furnished bis(trimethylsilylbutadiynyl)methanofullerene **10** in 39% yield. Its ^{13}C NMR spectrum showed four peaks (δ = 89.32, 87.57, 70.88, and 68.62) in the region characteristic for acetylenic C-atoms and a total of 17 distinct fullerene signals (16 between δ = 146 and 138 and one at δ = 74.41) indicating C_{2v} symmetry. The low-temperature (100 K) X-ray crystal structure of **10**,[2b] unambiguously proved the 6-6 closed structure of the methanofullerene.[11] The crucial 6-6 bond length between the bridgehead C-atoms is 1.574(3) Å, which is close to the calculated value of 1.55(1) for a 6-6 closed structure.[12] Compound **10** is very soluble in common organic solvents. During cyclic voltammetry or upon electrolysis, **10** undergoes reductive electrochemical polymerization to give an insoluble, air-stable, electrically conducting film on the platinum cathode surface.[2b] The structure and mechanism of formation of this polymeric film[13] is still under investigation. To explore the scope of this novel electrochemical polymerization reaction, we synthesized a number of structurally related bis(butadiynyl)methanofullerenes. For this purpose, oxidative coupling of **3** was carried out with five different monosubstituted acetylenes. With phenylacetylenes carrying strongly electron donating substituents (OMe, NMe_2) in the *para*-position, the corresponding bis(butadiynyl)methanofullerenes **11** and **12** could be isolated in 25% and 43% yield, respectively (*Scheme 2*). However, phenylacetylene itself gave only very low yields (< 5%), as did *t*-butylacetylene. With triisopropylsilylacetylene the expected product was formed in good yield (TLC, crude ^{1}H NMR), but its separation from large amounts of 1,4-bis(triisopropylsilyl)butadiyne, formed by homo-coupling, was nearly impossible. In case of **11** and **12**, flash chromatography was sufficient to separate the products from the accompanying homo-dimers. After recrystallization from toluene, compounds **11** and **12** were only scarcely soluble in CS_2, but nevertheless could be fully characterized. Their spectral data closely resemble those of **10**, *i.e.* four acetylenic and seventeen fullerene resonances were observed in the ^{13}C NMR spectra of each of the two compounds.



Scheme 2. Hetero-coupling reactions of **3** with monosubstituted acetylenes.

Hay coupling of **8** under the same conditions as mentioned for **3** afforded the unsymmetrically substituted derivative **13** in 49% yield (*Scheme 3*). This compound could also be prepared in 36% yield (53% based on reacted starting material) by coupling **8** with bromotrimethylsilylacetylene using $[PdCl_2(PPh_3)_2]$/CuI/TMEDA as a catalyst. The structure of **13** was easily identified from its ^{13}C NMR spectrum. A total of 30 resonances out of 32 expected was distinguishable for the fullerene carbons (29 between $\delta = 139$ and 147, one at $\delta = 75.39$), and the 10 expected non-fullerene resonances were clearly observed. The electrochemical behavior of compounds **11-13** is currently under investigation.



Scheme 3. Oxidative coupling reactions of mono-protected fullerene **8** under different reaction conditions.

Homo-coupling of monoprotected fullerene **8** using excess CuCl and TMEDA under an atmosphere of dry air gave the butadiyndiyl-linked "dimeric" methanofullerene **14** in 37% yield after 7 h at room temperature (*Scheme 3*).[2a, 14] In contrast to previously reported "dimeric" fullerene derivatives,[15] the black shiny crystals of **14** were reasonably soluble in cyclohexane, toluene, and CS_2, which permitted for the first time complete spectroscopic characterization of a dumbbell-shaped fullerene molecule. In the ^{13}C NMR spectrum (CS_2/C_6D_6 1:1), 31 fullerene resonances could be distinguished from which 30 appeared in the typical fullerene region and one at $\delta = 73.95$. The acetylenic carbon signals appeared at $\delta = 97.20$, 88.90, 75.31, and 69.72, and the methano bridge C-atom resonated at $\delta = 28.61$. The low temperature (100 K) centrosymmetric X-ray crystal structure of **14**, projected onto the mean molecular plane, is shown in *Fig. 1*. The numbering of the C_{60} skeleton used here refers to that introduced by Taylor.[16] Estimated standard deviations of bond lengths and bond angles, based on least-squares refinement are ca. 0.004 Å and 0.3°, respectively. Standard deviations (s) of mean values (given in parentheses) are based on the equation $s = [\Sigma_m(x_m - \langle x \rangle)^2/(m-1)]^{1/2}$.

The butadiyndiyl unit connecting the C_{60} spheres is practically linear, whereas the acetylenic fragments bonded to the triisopropylsilyl groups are bent appreciably towards the individual C_{60} skeletons. The bending, caused mainly by the crystal packing, is evident from the bond angles at C(62) and C(63), which are 172.7° and 174.6°, respectively. The plane of the cyclopropane ring is perpendicular (within 0.3°) to the plane defined by C(61), C(62), C(63), C(73), and C(74) and nearly bisects the bond angle C(62)-C(61)-C(73), which amounts to 118.1°. Bond lengths and bond angles of the cyclopropane ring and the acetylenic sub-units (see *Table 1* in Experimental Section) are in the expected range, and very close to the corresponding values determined in **10**.[2b]

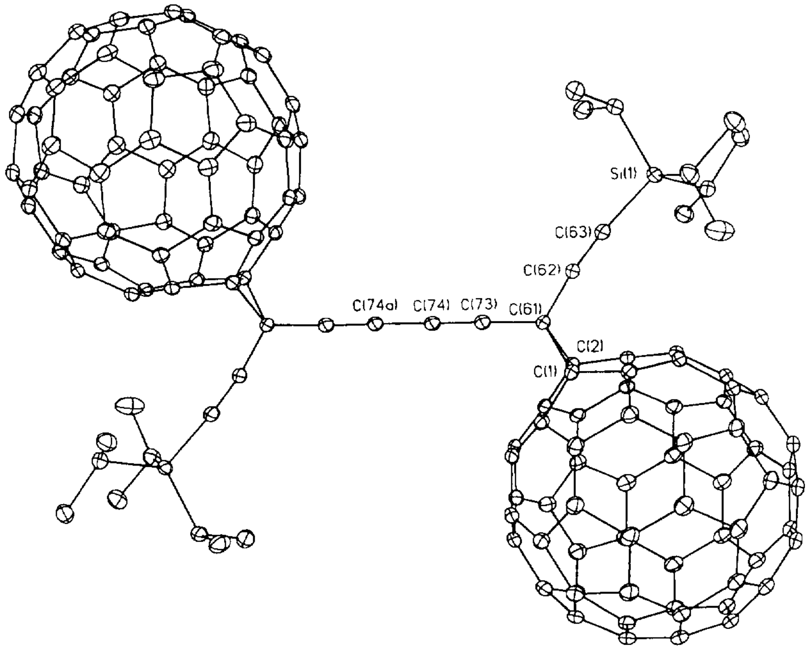


Figure 1. Low-temperature (100 K) X-ray crystal structure of the dumbbell-shaped fullerene derivative **14**. Vibrational ellipsoids are shown at the 30% probability level.

The unsubstituted C_{60} hemisphere exhibits a very regular geometry with mean 6-6 and 6-5 bond lengths of 1.391(5) Å and 1.450(5) Å, respectively. With respect to these mean values, the bridgehead C–C bond length (1.575 Å) increases by 0.184 Å, the 6-5 bonds containing C(1) and C(2) (see *Fig. 2*) by ca. 0.04 Å. The increase in bond length is accompanied by an increase of angular strain, as is obvious from the bond angles, listed in *Table 2* (see Experimental Section). At C(1) and C(2) the angles in question range from 105.3° to 116.4°, those at C(3), C(6), C(9), and C(12) from 107.8° to 123.4°, their average sums being 337.7° and 350.5°, respectively. While most five- and six-membered rings are practically planar, the rings containing the bridgehead C-atoms show appreciable deviations from planarity, as found in other fullerene structures. The two five-membered rings have an envelope conformation, *i.e.*, the bridgehead C-atoms are out of plane by ca. 0.15 Å with respect to the remaining four coplanar atoms. The two six-membered rings are slightly deformed towards a boat conformation, *i.e.*, C(3) and C(6), respectively C(9) and C(12) deviate by ca. 0.07 Å with respect to the remaining four coplanar atoms.

According to several fullerene studies,[17,18] the four 6-6 bonds on the edges of the bridged pyracylene sub-unit C(3)-C(4), C(5)-C(6), C(9)-C(10), C(11)-C(12), and the equatorial 6-6 bonds C(18)-C(36), C(27)-C(45) (not indicated in *Fig. 2*) have the highest reactivity towards nucleophiles. *Fig. 2* shows that the four shortest 6-6 bonds (1.378 Å to 1.385 Å) occur on the edges of the bridged pyracylene unit, in agreement with the X-ray crystal structure of **10**.[2b] This could suggest that the observed regioselectivity is connected with a slight decrease in bond length, or with a slight increase in bond order, respectively. However, such a relation is not perceptible for the two equatorial 6-6 bonds C(18)-C(36) and C(27)-C(45). In fact, their lengths (1.399 Å and 1.396 Å) are significantly larger (ca. 0.01 Å) than those of the other equatorial bonds C(22)-C(23) and C(31)-C(32), and also slightly larger than the mean 6-6 bond length derived from the unsubstituted C_{60} hemisphere. According to recent results, the observed regioselectivity of attack at 6-6 bonds in C_{70} fullerenes correlates with the degree of pyramidalization of the fullerene atoms, rather than with corresponding bond orders.[19] In the present analysis, the degree of pyramidalization *S* at an atom (expressed as the difference between 360° and the sum of three bond angles at that atom) has been estimated for the atoms involved in equatorial bonds. For the atom pairs C(18)-C(36) and C(27)-C(45), the corresponding *S*-value ranges from 11.2° to 12.1° (mean 11.6°), and for the pairs C(22)-C(23) and C(31)-C(32) from 11.8° to 12.2° (mean 12.1°), in other words, a correlation between bond reactivity and pyramidality as found for fullerene C_{70} is not observable here. It should be mentioned that the small systematic differences between bond lengths and *S*-values observed in this structure and that of **10**[2b] show the same trend. A theoretical explanation for the enhanced regioselectivity of nucleophilic additions, based on MO calculations as well as on the thermodynamic stability of C_{60} adducts, has been given by Hirsch *et al.*[17c]

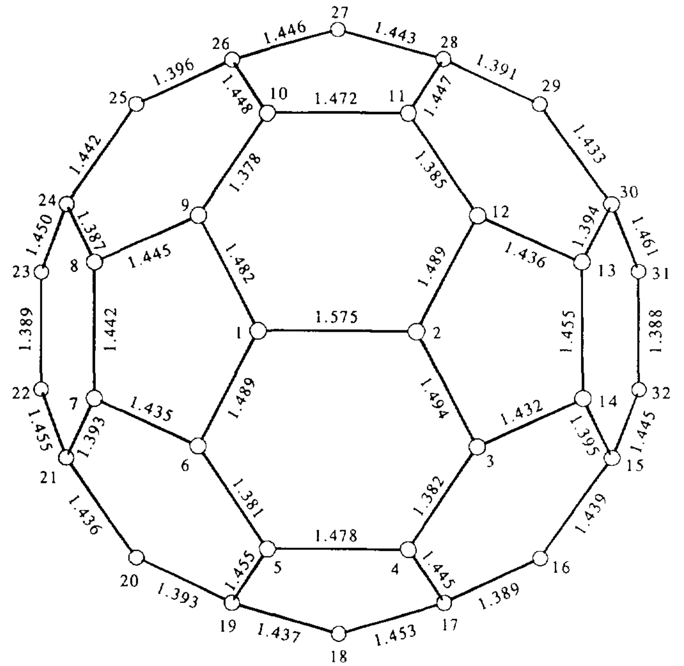
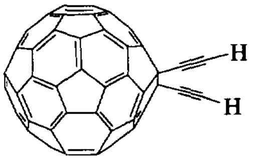


Figure 2. Bond lengths within the bridged hemisphere of **14**. Estimated standard deviations are ca. 0.004 Å.

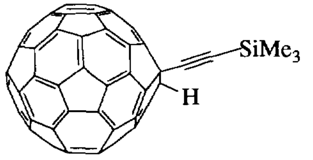
A comparison of the molecular geometry of **14** (*Figs. 1* and *2*) and **10**[2b] shows that the deformations at the C_{60} surface, induced by the different addends are almost the same in both molecules. Bridgehead C–C bond lengths agree within 0.001 Å, and the angular strain at C(1) and C(2) (based on the sum of three bond angles) within 0.9°. The remaining bond lengths and bond angles of the bridged pyracylene sub-units also agree within one or two estimated standard deviations. Based on these small differences between **14** and **10** there is no structural evidence that any electronic interaction exists between the two fullerene moieties in dumbbell **14**. This notion is further supported by the UV-data of **14**[2a] and preliminary results from electrochemical investigations.

2.2. *Progress Towards the Synthesis of 1,2-Diethynyl-1,2-dihydrofullerene[60] (15)*

Just as the fullerene end-capped macrocycles of type **1** can theoretically be built up by oxidative cyclooligomerizations of diethynylmethanofullerene **3**,[20] macropolyynes **2** can potentially be synthesized in the same way starting from diethynylfullerene **15**. In an earlier communication,[2a] we reported on the synthesis of hydrofullerene **16**.[21] Here we describe first attempts directed at the synthesis of diethynylated **15**.

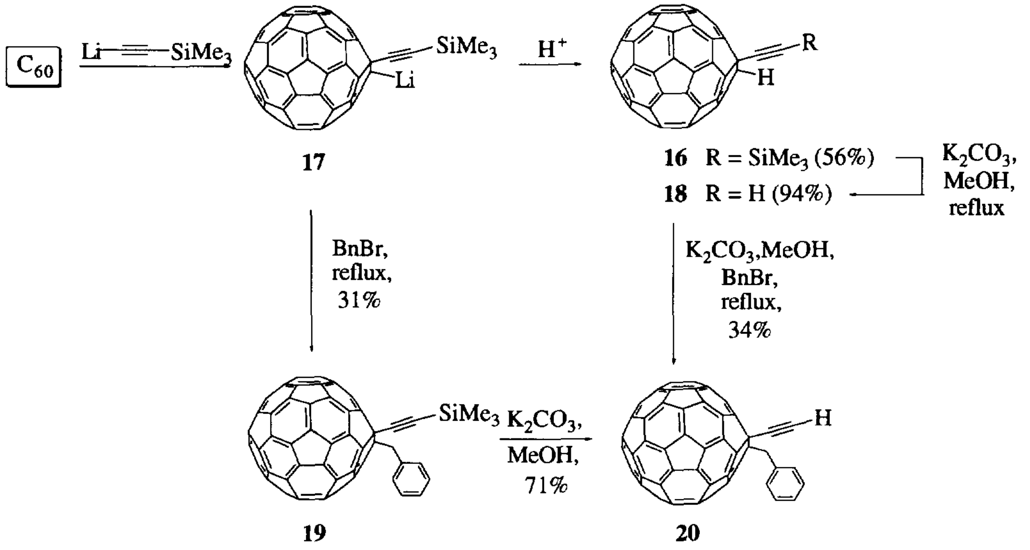


15



16

2.2.1. Nucleophilic Addition of Acetylides to C_{60}. When a solution of C_{60} in toluene was treated with chloromagnesiumacetylide at room temperature under anhydrous conditions, formation of a product could not be observed even with a large excess of reagent or after prolonged reaction times. However, treatment of C_{60} with lithium trimethylsilylacetylide in toluene gave a black precipitate, which, upon quenching with acetic acid, afforded hydrofullerene **16** as a brown solid in 58% yield (*Scheme 4*). The reaction is considerably slower compared to the addition of aromatic or aliphatic organolithium compounds and Grignard reagents to fullerenes.[22] Compound **16** is very soluble in CS_2 and toluene, moderately soluble in $CHCl_3$, CH_2Cl_2, and THF, and almost insoluble in cyclohexane. Its purification was severely complicated by the small difference in polarity between **16** and C_{60}. Pure **16** could only be obtained after repeated flash chromatography with hot cyclohexane followed by recrystallization from CS_2/pentane. The structure of **16** is evident from its spectroscopic data. The singlet at $\delta = 6.92$ in the ^1H NMR spectrum (CS_2) is characteristic of a proton directly attached to the carbon sphere. The 32 fullerene resonances in the ^{13}C NMR spectrum clearly show that addition has taken place specifically at a 6-6 double bond. The two newly formed sp^3-C-atom centers resonate at $\delta = 61.82$ (C_{sp^3}-H) and $\delta = 55.10$ (C_{sp^3}-C_{sp}), the two acetylenic C-atoms at $\delta = 107.33$ and 88.15.



Scheme 4. Synthesis of 1-hydro-2-trimethylsilylethynylfullerene **16** and some of its derivatives.

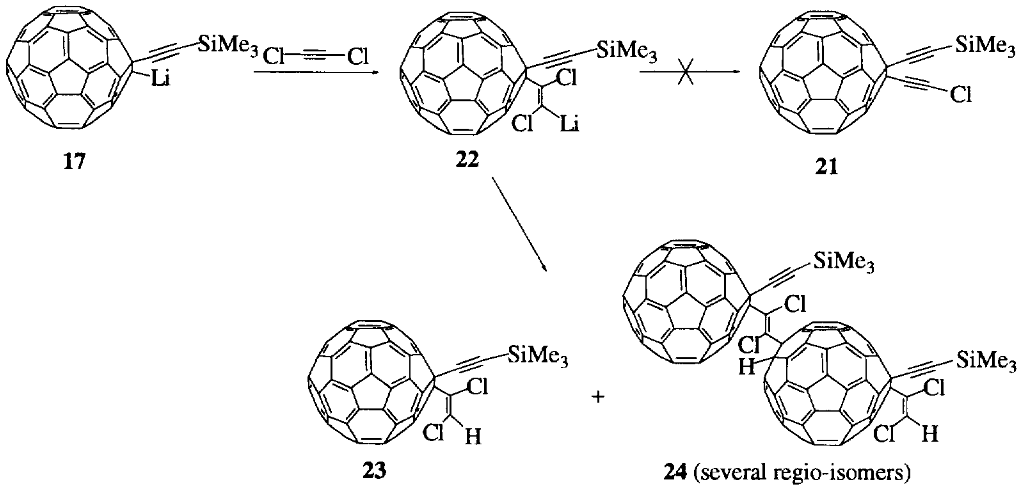
The proton directly attached to the carbon sphere is highly acidic as a result of the strong electron affinity of the fullerene sphere. Fagan *et al.*[23] determined a $pK_a = 5.7$ for 1-hydro-2-*t*-butylfullerene[60] in Me_2SO. This value seems to be consistent with our finding that **16** can be readily deprotonated with K_2CO_3 in Me_2SO as is evident from the deep green color of the resulting solution, which is characteristic for the formed anion. However, the acidity of **16** strongly depends on the base and solvent. For instance, K_2CO_3 is not strong enough to deprotonate **16** in THF, but NaH is. However, in toluene even NaH ($pK_a = 35$) does not deprotonate **16**, but addition of DBU, a much weaker base ($pK_a = 24.3$ in MeCN), readily turns the solution dark green. At this point even H_2O ($pK_a = 15.7$) does not quench the anion. However, addition of H_2O to a solution of 1-lithio-2-trimethylsilylethynylfullerene (**17**) in toluene immediately quenches the anion. Apparently, the stability of the fulleride anion strongly depends on the ability of the solvent to solvate the cation. Interestingly, compound **16** can only be desilylated after prolonged reflux with methanolic potassium carbonate to give **18** in 94% yield. Presumably, the negative charge on the anion makes the Si-atom less susceptible to attack by methoxide. Compound **18** is only soluble in CS_2 and chlorobenzene.

Fullerene anions have previously been reported to react with simple electrophiles, such as methyl iodide.[23] Benzyl derivative **19** was prepared in 31% yield by refluxing **17** with benzyl bromide in THF for 2 h. The compound has increased solubility in common organic solvents like $CHCl_3$ and CH_2Cl_2 compared to the corresponding hydrofullerene **16**. It forms large single crystals from benzene, but all attempts to determine its crystal structure failed. Desilylation using standard reaction conditions gave in 71% yield compound **20**, which is still reasonably soluble in toluene.

In an effort to synthesize diethynylfullerene **15**, we studied the reactivity of **16** towards electrophiles which can be used for the introduction of a second acetylene unit. However, synthetic equivalents of "$H\text{-}C{\equiv}C^+$" are rare. The most direct examples are the iodonium acetylides[24] and the haloalkynes.[25] A less direct approach to the introduction of a C≡C triple bond is provided by the dibromo-olefination of aldehydes followed by elimination/metallation and quenching with protons or electrophiles.[26]

The reaction of **17** with dichloroacetylene[27] reached completion in a few hours at room temperature. Neither of the two main products formed could be fully characterized, but it seems that the desired product **21** was not formed. Based on mass spectrometric analysis, we tentatively assign structures **23** (FAB-MS: *m/z* 914, M^+; $C_{67}H_{10}Cl_2Si$ requires 914) and **24** (matrix-assisted laser desorption time-of-flight (MALDI-TOF) MS: *m/z* 1828, M^+, $^{12}C_{133}{}^{13}CH_{20}Cl_4Si_2$ requires 1827) to the two compounds formed (*Scheme 5*). Compound **23** was the minor product and showed a higher R_f value and higher solubility than **24** which is the major product. It seems that the vinylic anion intermediate **22** does not eliminate chloride, but adds to another fullerene or persists until it is protonated. Experiments carried out in the presence of weak acids that can protonate the vinylic anion intermediate were unsuccessful.

(Trimethylsilylethynyl)(phenyl)iodonium triflate[28] reacts very rapidly with **17**, even at -78 °C, to give an extremely complex mixture of products. The iodonium salt appears to behave as an one-electron oxidant, leading to unselective free-radical chemistry.



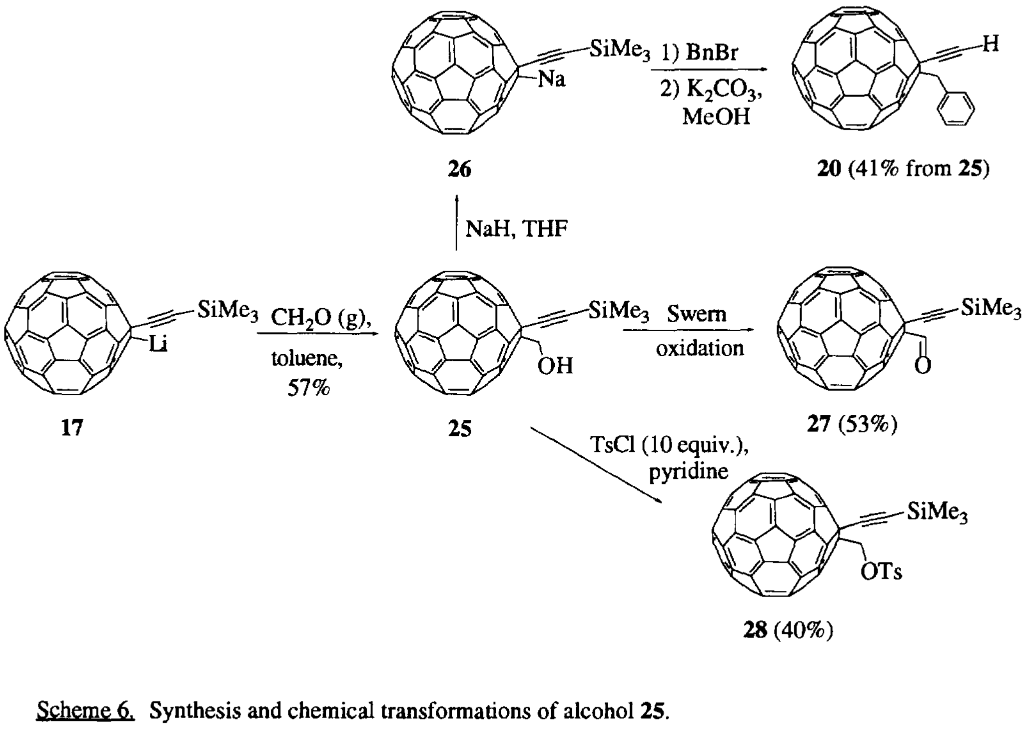
Scheme 5. Products in the reaction of 1-lithio-2-trimethylsilylethynylfullerene **17** with dichloroacetylene.

In order to explore the dibromo-olefination of aldehydes as a way to introduce acetylene functionality, we investigated the reaction of **17** with *N,N*-dimethylformamide (DMF) and methyl formate. In neither of the two cases the formation of any product could be observed, not even after one week of reflux in THF.

Bubbling formaldehyde gas[29] through a solution of **17** in toluene at 0 °C for 5 min gave the primary alcohol **25** in 57% yield (*Scheme 6*). In contrast to hydrofullerene **16**, alcohol **25** could be purified relatively easily from residual C_{60} by flash chromatography due to the large difference in polarity. The ^1H NMR spectrum of **25** in $CDCl_3$ showed a doublet at $\delta = 5.64$ and a triplet at $\delta = 4.20$ for the protons of the CH_2OH

group. The ^{13}C NMR spectrum displayed the expected 32 resonances for a fullerene derivative with C_s symmetry.

Alcohol **25** is an air-stable compound that did not show any decomposition after several hours of reflux in toluene. In a weakly basic solvent like pyridine, it could be kept for several days. However, under strongly basic conditions, formaldehyde was eliminated rapidly. Treatment of **25** in dry THF with NaH showed quantitative conversion to the sodium salt **26** after several min at 0 °C. The same conversion was observed with NaH in toluene, with the exception that **16** was formed instead of its sodium salt **26**. The instability of alcohol **25** results from the fact that the fullerene anion is a very good leaving group, as was observed before.[30] It is therefore even more surprising that alcohol **25** is actually formed under the conditions mentioned (*vide supra*). This must be related to the much higher basicity and, consequently, the worse leaving group ability of lithium salt **17** in a non-coordinating solvent like toluene. Elimination of formaldehyde was also observed when methanol was added to a solution of **25** in toluene. The reaction seems to be catalyzed by small (acidic) impurities, since it was never observed with recrystallized samples of **25**. The quick conversion of alcohol **25** into hydrofullerene **16** provides an easy route to obtain highly pure samples of the latter.



Scheme 6. Synthesis and chemical transformations of alcohol **25**.

Starting from alcohol **25**, benzyl derivative **20** (*Scheme 4*) can now be synthesized in a one-pot procedure by successive treatment with NaH in THF, removal of NaH, reflux with benzyl bromide, and finally proto-desilylation with K_2CO_3 and methanol in an overall yield of 41%. Monitoring the reaction by TLC revealed that a small amount of C_{60} was formed during the reaction with benzyl bromide at reflux temperature. Apparently, the addition of the acetylide anion to C_{60} is reversible at this temperature, something that was not observed before for nucleophilic additions of organometallic compounds to fullerenes. This observation is certainly interesting in terms of using the addition of silyl-protected acetylides to C_{60} for the introduction of a removable solubilizing group and will be studied in more detail.

Aldehyde **27** was prepared in 53% yield via Swern oxidation of alcohol **25**. Diagnostic is the singlet at $\delta = 11.3$ in the ^1H NMR spectrum. Oxidation with pyridinium dichromate (PDC) also gave the aldehyde, but the reaction did not go to completion. Aldehyde **27** is even less stable than alcohol **25**. It readily looses formaldehyde upon contact with MeOH at room temperature to give hydrofullerene **16**. Methanol is believed to attack the carbonyl group via an addition-elimination mechanism with the fullerene anion as a leaving group. As a result of the very good leaving group ability of the fullerene anion, aldehyde **27** is comparable in reactivity to an activated ester. Likewise, the reaction with methanol is analogous to a transacylation reaction. This type of side reactions greatly limited the use of aldehyde **27** in further transformations.

Attempted dibromo-olefination of **27** with $CBr_4/PPh_3/Zn$ (50 equiv.) in CH_2Cl_2 was not successful. After 1 h at room temperature, which is normally enough to drive the reaction to completion,[26c] only starting material was recovered. Even after 48 h the desired dibromo-olefination product was not formed, but instead the starting material had decomposed. The low reactivity of aldehyde **27** in this reaction might be due to the high sterical shielding of the reaction center.

Another possible way of introducing dibromo-olefin functionality consists in the reaction of **17** with α,α–dibromoacetaldehyde to give the fullerene-substituted dibromoethanol, followed by elimination of TsOH from the corresponding tosylate. As a model reaction the tosylation of **25** was investigated. Treatment of **25** with 1 equiv. of *p*-toluenesulfonyl chloride in CH_2Cl_2 at room temperature was not effective. Only the reaction in pyridine with excess (10 equiv.) *p*-toluenesulfonyl chloride afforded tosylate **28** in 40% yield after 3 d. A total of 30 of the 32 fullerene resonances (28 between $\delta = 134$ and 153 and two at $\delta = 63.83$ and 58.35) could be clearly distinguished in the ^{13}C NMR spectrum. Reactions of **17** with any aldehyde other than formaldehyde have so far been unsuccessful. Generally, the reactions were much slower compared to that with formaldehyde, which can be attributed, at least partially, to the extreme steric crowding around the fullerene nucleophilic center.

3. CONCLUSIONS

The synthesis of both symmetrically and unsymmetrically silyl-protected diethynylmethanofullerenes is well established now. Oxidative acetylenic coupling reactions under Hay conditions are applicable to fullerene chemistry and should provide a successful approach to the synthesis of carbon allotropes **1**.[20] The synthesis of a number of substituted trimethylsilylethynylfullerenes has now been realized, some of which exhibit very interesting chemical reactivity. This contributes to a better understanding of the fascinating chemistry of fullerenes, and most importantly for our program, generates new perspectives for the preparation of novel fullerene-acetylene hybrid carbon allotropes.

4. EXPERIMENTAL SECTION

General. Reagents used were reagent-grade commercials. C_{60} was isolated from the commercially available C_{60}/C_{70} mixture according to a previously reported method.[9a] 3-Bromo-1,5-bis(trimethylsilyl)penta-1,4-diyne (**5**) and 1-(triisopropylsilyl)-5-(trimethylsilyl)penta-1,4-diyn-3-one were prepared according to literature procedures.[6,26c,31]. 4(-Methoxyphenyl)acetylene and 4-[(*N,N*-dimethylamino)phenyl]acetylene were prepared according to the method of Higahara.[32] All reactions were performed in standard glassware under an inert atmosphere of N_2 or Ar. Organometallic reactions were carried out in flame-dried Schlenk tubes flushed with N_2 (5 x) prior to the reaction. Solvents were transferred using cannula technique and deoxygenated prior to the reaction. Toluene was pre-dried over NaH and freshly distilled from Na/benzophenone. THF was freshly distilled from Na/benzophenone. Evaporation and concentration *in vacuo* was done at water aspirator pressure, drying *in vacuo* at 10^{-2} Torr. Silica gel 60 (230-400 mesh, 0.040-0.063 mm) was purchased from E. Merck. Thin layer chromatography (TLC) was performed on glass sheets coated with silica gel 60 F_{254} purchased from E. Merck; visualization by UV light. Melting points were measured on a Büchi apparatus and are uncorrected. UV/VIS spectra (λ_{max} in nm (ε)) were measured on a Varian Cary-5 spectrophotometer. IR spectra (cm^{-1}) were measured on a Perkin Elmer 580 instrument. NMR spectra were recorded on a Bruker AM 500 (^{13}C) and on a Varian Gemini 300 or 200 MHz (^{1}H) at 296 or 300 K, with solvent peaks as reference. Mass spectra (*m/z* (%)) were taken on a VG Tribrid instrument for EI, a VG ZAB 2SEQ instrument for FAB with 3-nitrobenzyl alcohol as a matrix, or a Bruker REFLEX spectrometer for MALDI-TOF with 2,5-dihydroxybenzoic acid as a matrix. Only the most intense peaks in the molecular ion clusters are reported. Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH Zürich.

61,61-Bis[(trimethylsilyl)ethynyl]-1,2-dihydro-1,2-methanofullerene[60] (4). To a solution of C_{60} (500 mg, 0.694 mmol) and **5** (300 µL, 1.15 mmol) in toluene (500 mL) was added DBU (300 µL, 2.01 mmol), and the solution was stirred at 20 °C. After 2 h the reaction mixture was quenched with acetic acid (1.0 mL) and filtered over a short plug of silica gel. After removal of the solvent the crude product was recrystallized twice from hot cyclohexane. Unreacted C_{60} was removed by dissolving the black crystals in THF followed by filtration over a tight plug of Celite. Evaporation of the filtrate gave pure **4** (335 mg, 52% yield, 56% based on reacted C_{60}) as a brown solid: m.p. > 300 °C. IR (KBr): 2954 (w), 2922 (w), 2895 (w), 2845 (w), 2171 (w), 1427 (w), 1247 (m), 843 (s), 758 (m), 525 (m). ^{1}H NMR ($CS_2/CDCl_3$ 1:1, 200 MHz): 0.35 (s, 18 H). ^{13}C NMR ($CS_2/(CD_3)_2CO$ capillary, 125 MHz): 0.01, 27.47, 75.60, 91.08, 96.78, 139.05, 141.26, 142.23, 142.48, 143.03, 143.12, 143.15, 144.16, 144.80, 144.83, 144.96, 145.17, 145.48, 145.49, 145.71, 146.34. UV/Vis (CH_2Cl_2): 257 (112 000), 329 (38 000), 435 (2 200), 489 (1 600), 687 (250). FAB-MS: 720 (100, C_{60}^+), 927 [80, $(M + H)^+$]. Anal. calc. for $C_{71}H_{18}Si_2$ (927.11): C 91.98, H 1.96; found: C 92.28, H 2.20.

1-(Triisopropylsilyl)-5-(trimethylsilyl)penta-1,4-diyne-3-one (*p*-toluenesulfonyl)hydrazone (7). A solution of 1-(triisopropylsilyl)-5-(trimethylsilyl)penta-1,4-diyn-3-one (6.0 g, 19.6 mmol) and (*p*-toluenesulfonyl)hydrazide (3.64 g, 19.6 mmol) in acetic acid (60 mL) was refluxed for 2 h. The resulting orange solution was poured into cold water (300 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated to dryness. Column chromatography (SiO_2, hexane/CH_2Cl_2 2:1) followed by recrystallization from hexane yielded pure **7** (5.3 g, 57% yield, 1:1 mixture of *cis* and *trans* isomers) as pale yellow crystals: m.p. 89 °C. IR (neat): 3181 (m), 2945 (s), 2866 (s), 2156 (w), 1635 (m), 1597 (m), 1463 (s), 1386 (s), 1350 (s), 1253 (s), 1171 (s), 1086 (s), 1011 (w), 997 (m), 927 (s), 878 (s), 843 (s), 761 (m), 680 (s). ^1H NMR ($CDCl_3$, 200 MHz): 0.17 (s, 9 H), 0.24 (s, 9 H), 1.06 (s, 21 H), 1.10 (s, 21 H), 2.39 (s, 6 H), 7.29 (m, 4 H), 7.79 (d, J = 8.0, 2 H), 7.82 (d, J = 8.0, 2 H), 8.71 (bs, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): -0.45, 11.11, 11.31, 18.68, 21.79, 92.61, 94.38, 96.01, 98.26, 98.48, 100.68, 108.31, 110.43, 112.37, 119.58, 119.65, 128.16, 128.28, 130.09, 130.18, 135.60, 144.97, 145.02. EI-MS (70 eV): 73 (100, Me_3Si^+), 431 [4, $(M - i\text{-Pr})^+$], 474 (1, M^+). Anal. calc. for $C_{24}H_{38}N_2O_2Si_2S$ (474.81): C 60.71, H 8.07, N 5.90, S 6.75; found: C 60.77, H 8.03, N 5.70, S 6.77.

61-[(Triisopropylsilyl)ethynyl]-61-[(trimethylsilyl)ethynyl]-1,2-dihydro-1,2-methanofullerene[60] (6). To a solution of **7** (700 mg, 1.48 mmol) in dry benzene (70 mL) was slowly added *n*-BuLi (0.9 mL 1.6 M, 1.48 mmol), and the resulting solution was stirred at 20 °C for 30 min. The mixture was added to a solution of C_{60} (400 mg, 0.55 mmol) in dry benzene (400 mL) at 20 °C, and the resulting solution was refluxed for 3 h. The solvent was evaporated and flash chromatography (SiO_2, hexane) followed by recrystallization from CS_2/Et_2O yielded pure **6** (298 mg, 53% yield) as black crystals: m.p. > 270 °C. IR (KBr): 2939 (s), 2856 (s), 2167 (w), 1461 (m), 1422 (m), 1248 (m), 843 (m), 525 (s). ^1H NMR ($CDCl_3$, 200 MHz): 0.33 (s, 9 H), 1.19 (s, 21 H). ^{13}C NMR ($CDCl_3$, 125 MHz): 0.00, 11.34, 18.60, 32.24, 75.58, 87.32, 90.69, 97.25, 98.18, 139.00, 139.24, 141.02, 141.05, 142.09, 142.10, 142.23, 142.36, 142.86, 142.88, 142.93, 142.95, 142.96, 142.99, 144.01, 144.02, 144.70, 144.75, 144.81, 144.85, 145.05, 145.36, 145.37, 145.38, 145.67, 145.74, 146.24, 146.41. UV/Vis (CH_2Cl_2): 258 (107 000), 329 (35 500), 436 (2 200), 488 (1 500), 687 (100). FAB-MS: 73 (100, Me_3Si^+), 720 (43, C_{60}^+), 1011 [4, $(M + H)^+$].

61, 61-Diethynyl-1,2-dihydro-1,2-methanofullerene[60] (3). A solution of **4** (220 mg, 0.237 mmol) and K_2CO_3 (50 mg, 0.36 mmol) in THF/MeOH 10:1 (220 mL) was stirred at 20 °C until TLC analysis showed no other compounds than **3** (R_f = 0.58, SiO_2, cyclohexane). Toluene (50 mL) was added, and the mixture was filtered over a short plug of silica gel and evaporated to dryness. The crude material was purified by flash chromatography (SiO_2, CS_2) and recrystallized from CS_2/pentane to afford pure **3** (153 mg, 83% yield) as black crystals: m.p. > 300 °C. IR (KBr): 3291 (w), 2122 (w), 1425 (w), 1182 (w), 869 (w), 743 (m), 660 (m), 654 (m), 622 (m), 525 (s). ^1H NMR ($CS_2/CDCl_3$ 1:1, 200 MHz): 2.87 (s, 2 H). ^{13}C NMR ($CS_2/(CD_3)_2CO$ capillary, 125 MHz): 74.52, 75.82, 139.10, 141.06, 142.04, 142.26, 142.85, 142.95, 143.94, 144.56, 144.64, 144.81, 144.99, 145.30, 145.41, 145.67. UV/Vis (CS_2): 404 (4 000), 432 (2 900), 476 (1 800), 686 (250). FAB-MS: 720 (100, C_{60}^+), 782 (21, M^+).

61-Ethynyl-61-[(triisopropylsilyl)ethynyl]-1,2-dihydro-1,2-methanofullerene[60] (8). To a solution of **6** (298 mg, 0.295 mmol) in THF/MeOH (250 mL/70 mL) was added a solution of K_2CO_3 (150 mg, 1.09 mmol) in H_2O (3 mL), and the resulting mixture was stirred at 20 °C for 30 min. Subsequently, the solution was concentrated to a volume of 10 mL and partitioned between toluene (200 mL) and H_2O (200 mL). The organic layer was washed with H_2O (2 x 100 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. Flash chromatography (SiO_2, hexane) followed by recrystallization from CS_2/Et_2O gave pure **8** (191 mg, 69% yield) as bronze flakes: m.p. > 270 °C. IR (KBr): 3289 (m), 2922 (s), 2856 (s), 2167 (w), 2119 (w), 1456 (m), 1422 (m), 672 (m), 522 (s). ^{1}H NMR ($CDCl_3$, 200 MHz): 1.20 (s, 21 H), 2.88 (s, 1 H). ^{13}C NMR (CS_2/C_6D_6 1:1, 125 MHz): 11.66, 18.95, 29.51, 73.35, 74.94, 76.47, 87.61, 98.21, 139.42, 141.36, 141.38, 142.34, 142.36, 142.41, 142.61, 143.18, 143.28 (several overlapping peaks), 144.26, 144.28, 144.89, 144.97, 145.15, 145.19, 145.30, 145.65 (several overlapping peaks), 145.78, 146.12, 146.21. UV/Vis (CH_2Cl_2): 258 (148 000), 328 (45 700), 406 (4 700), 434 (3 200), 493 (2 200), 688 (900). FAB-MS: 720 (100, C_{60}^+), 939 [21, $(M + H)^+$].

61-Ethynyl-61-[(trimethylsilyl)ethynyl]-1,2-dihydro-1,2-methanofullerene[60] (9). To a solution of **4** (50 mg, 0.054 mmol) in THF/MeOH 10:1 (66 mL) was added a solution of K_2CO_3 (56 mg, 0.4 mmol) in water (1.5 mL), and the resulting mixture was stirred at 20 °C for 90 min after which TLC analysis showed that **9** was the main product. Acetic acid was added (0.1 mL), and the solution was evaporated to dryness. Flash chromatography (SiO_2, hexane/THF 97:3) yielded mono-deprotected fullerene **9** together with **3** (7.9 mg, 18% yield). Crystallization from CS_2/pentane finally gave pure **9** (16.3 mg, 35% yield, 41% based on reacted starting material) as black crystals: m.p. > 270 °C. IR (KBr): 3285 (m), 2955 (s), 2174 (w), 1509 (m), 1427 (m), 1247 (s), 1066 (m), 843 (s), 525 (s). ^{1}H NMR ($CDCl_3/CS_2$ 1:1, 200 MHz): 0.36 (s, 9 H), 2.85 (s, 1 H). ^{13}C NMR ($CDCl_3/CS_2$, 1:1, 125 MHz): -0.15, 27.20, 73.28, 74.67, 76.11, 91.06, 96.47, 138.82, 138.94, 140.95, 140.99, 141.93, 141.96, 142.14, 142.22, 142.74, 142.76, 142.84, 142.85 (several overlapping peaks), 142.86, 143.86, 144.46, 144.49, 144.56 (several overlapping peaks), 144.70, 144.72, 144.91, 145.22, 145.36, 145.55, 145.88. UV/Vis (CH_2Cl_2): 257 (119 500), 328 (40 100), 433 (2 600), 481 (1 500). FAB-MS: 720 (57, C_{60}^+), 855 [22, $(M+ H)^+$].

61,61-Bis[(trimethylsilyl)butadiynyl]-1,2-dihydro-1,2-methanofullerene[60] (10). To a vigorously stirred solution of **3** (57 mg, 73 µmol) in dry chlorobenzene (400 mL) in a 2 L three-necked flask (*not* under N_2), equipped with a $CaCl_2$-tube, was added successively CuCl (2.15 g, 21.8 mmol), trimethylsilylacetylene (200 µL, 1.46 mmol) and TMEDA (3.3 mL, 21.8 mmol). Upon the addition of TMEDA the reaction mixture turned dark green, which indicated that the catalyst was formed. A total of 12 portions of trimethylsilylacetylene were added over the next 30 min (40 µL, 0.29 mmol every 2.5 min), and the reaction mixture was stirred for another 1.5 h. Subsequently, it was quenched with 1N HCl (250 mL) and filtered over Celite. The organic layer was washed with H_2O (3 x 100 mL) and brine (100 mL), dried over $MgSO_4$, and filtered over a short silica plug of silica gel. After removal of the solvent *in vacuo* ($T < 30$ °C !) the crude material was washed with pentane, which removed most of the accompanying 1,4-bis(trimethylsilyl)butadiyne. Recrystallization from CS_2/pentane gave pure **10** (28 mg, 39% yield) as a black solid: m.p. > 300 °C. IR (KBr): 2953 (w), 2894 (w), 2105 (w), 1513 (w), 1427 (w), 1248 (m), 1184 (w), 912 (m), 844 (s), 758 (m), 742 (m), 526 (s). ^{1}H NMR ($CS_2/(CD_3)_2CO$ capillary, 500 MHz): 0.24 (s, 18 H). ^{13}C NMR ($CS_2/(CD_3)_2CO$ capillary, 125 MHz): -0.65, 27.23, 68.62, 70.88, 74.41, 87.57, 89.32, 138.84, 140.89, 141.76, 142.04, 142.53, 142.68, 142.71, 143.70, 144.28, 144.40, 144.70, 144.74, 144.84, 145.03, 145.08, 145.10. UV/Vis (CH_2Cl_2): 256 (127 000), 329 (40 700), 435 (2 200), 487 (1 600), 687 (170). FAB-MS: 720 (100, C_{60}^+), 976 [2, $(M + H)^+$, $^{12}C_{74}{}^{13}CH_{19}Si_2$]. Anal. calc. for $C_{75}H_{18}Si_2$ (975.15): C 92.38, H 1.86; found: C 92.23, H 1.95.

61,61-Bis[(4-methoxyphenyl)butadiynyl]-1,2-dihydro-1,2-methanofullerene[60] (11). The reaction was carried out according to the procedure described for **10**, using **3** (90 mg, 0.115 mmol), 4-(methoxyphenyl)acetylene (300 µL, 2.3 mmol initially; 60 µL, 0.46 mmol every 2.5 min during 30 min), CuCl (5.0 g, 50.5 mmol), TMEDA (6.85 mL, 45.3 mmol), and chlorobenzene (700 mL). The crude material was dissolved in toluene (20 mL), insoluble material was filtered off, and cyclohexane (180 mL) was added. The solution was loaded on a column (SiO_2), and the product was eluted with cyclohexane/toluene 70:30. All product containing fractions were collected, evaporated down to a volume of 5-10 mL ($T < 30$ °C !), and stored at -20 °C for 16 h. The precipitated solid was filtered off and extensively washed with ether, until a black solid remained (40 mg). Flash chromatography of the filtrate (SiO_2 60 H, cyclohexane/toluene 70:30) afforded another 5 mg of pure **11**. A final recrystallization from toluene at -20 °C gave pure **11** (30 mg, 25% yield) as black crystals: m.p. > 300 °C. IR (KBr): 2959 (w), 2928 (w), 2857 (w), 2228 (w), 1731 (m), 1643 (m), 1602 (s), 1509 (s), 1251 (s), 1170 (m), 1030 (m), 829 (s), 742 (w), 526 (s). ^1H NMR ($CS_2/(CD_3)_2CO$ capillary, 500 MHz): 3.78 (s, 6 H), 6.76 (d, $J = 8.9$, 4 H), 7.40 (d, $J = 8.9$, 4 H). ^{13}C NMR ($CS_2/(CD_3)_2CO$ capillary, 125 MHz): 54.77, 71.20, 73.43, 73.55, 75.31, 80.47, 113.05, 114.10, 134.42, 139.08, 141.09, 141.98, 142.32, 142.74, 142.87, 142.92, 143.93, 144.55, 144.60, 144.87, 145.01, 145.28, 145.39, 160.44. UV/Vis (CS_2): 515 (sh, 2 000), 698 (250). FAB-MS: 720 (100, C_{60}^+), 1044 [10, $(M + H)^+$, ($^{12}C_{82}{}^{13}CH_{15}O_2$].

61,61-Bis{[4-(*N,N*-dimethylamino)phenyl]butadiynyl}-1,2-dihydro-1,2-methano-fullerene[60] (12). The reaction was carried out according to the procedure described for **10**, using **3** (75 mg, 96 µmol), 4-[(*N,N*-dimethylamino)phenyl]acetylene (300 mg, 1.92 mmol initially; 60 mg, 0.38 mmol every 2.5 min during 30 min), CuCl (3.0 g, 30 mmol), TMEDA (4.5 mL, 30 mmol), and chlorobenzene (500 mL). The crude material was taken up in CS_2 (50 mL), insoluble material was filtered off, and the dark red solution was loaded on a column (SiO_2, cyclohexane/toluene 9:1). After flushing the column with CS_2 to remove apolar impurities, the product was eluted with cyclohexane/toluene 7:3. All product containing fractions were collected, evaporated down to a volume of 5 - 10 mL ($T < 30$ °C !) and stored at -20 °C overnight. The crystals formed were filtered off and dried at high vacuum (10^{-7} mbar) to give pure **12** (45 mg, 44% yield) as black crystals: m.p. > 300 °C. IR (KBr): 2885 (w), 2849 (w), 2798 (w), 2211 (m), 2137 (w), 1600 (s), 1519 (m), 1440 (w), 1426 (w), 1361 (m), 1223 (w), 1185 (m), 1163 (w), 1060 (w), 942 (w), 811 (m), 740 (w), 586 (w), 555 (w), 524 (s). ^1H NMR ($CS_2/(CD_3)_2CO$ capillary, 500 MHz): 3.01 (s, 12 H), 6.52 (m, 4 H), 7.30 (m, 4 H). ^{13}C NMR ($CS_2/(CD_3)_2CO$ capillary, 125 MHz): 39.77, 71.74, 73.13, 73.32, 75.74, 82.04, 107.72, 111.64, 134.18, 139.08, 141.02, 141.97, 142.36, 142.68, 142.81, 142.90, 143.93, 144.57, 144.62, 144.80, 144.96, 145.24, 145.49, 145.72, 150.17. UV/Vis (CS_2): 438 (4 800), 483 (5 200), 633 (sh, 630), 702 (280). Anal. calc. for $C_{85}H_{20}N_2$ (1069.12): C 95.49, H 1.89, N 2.62; found: C 95.40, H 1.86, N 2.65.

61-[(Triisopropylsilyl)ethynyl]-61-[(trimethylsilyl)butadiynyl]-1,2-dihydro-1,2-methanofullerene[60] (13). a) From **8** and trimethylsilylacetylene. To **8** (81 mg, 0.086 mmol), trimethylsilylacetylene (845 mg, 8.6 mmol), and CuCl (426 mg, 4.3 mmol) in CH_2Cl_2 (250 mL) was added TMEDA (500 mg, 4.3 mmol), and the mixture was vigorously stirred for 4 h in the presence of dry air. The resulting mixture was filtered through a pad of silica gel (toluene), and the solvent was evaporated. Flash chromatography (SiO_2, hexane) followed by recrystallization from CS_2/pentane yielded pure **13** (44 mg, 49%

yield) as black crystals: m.p. > 270 °C. IR (KBr): 2933 (s), 2856 (s), 2178 (w), 2100 (w), 1459 (m), 1248 (m), 843 (s), 526 (s). ^{1}H NMR ($CDCl_3$, 200 MHz): 0.30 (s, 9 H), 1.20 (s, 21 H). ^{13}C NMR (CS_2/C_6D_6 1:1, 125 MHz): -0.40, 11.89, 19.10, 28.64, 70.66, 70.76, 75.39, 88.23, 88.50, 89.49, 97.82, 139.41, 139.56, 141.36, 141.45, 142.36, 142.42 (2x), 142.79, 143.10, 143.23, 143.26, 143.30, 143.32, 143.33, 144.31, 144.32, 144.98, 145.00, 145.04, 145.18, 145.33, 145.40, 145.69, 145.70, 145.73, 145.79, 145.81, 145.83, 146.16. UV/Vis (CH_2Cl_2): 256 (123 700), 329 (40 900), 436 (2 400), 488 (1 700), 687 (240). FAB-MS: 73 (100, Me_3Si^+), 720 (13, C_{60}^+), 1035 [1, $(M + H)^+$].

b) From **8** and bromotrimethylsilylacetylene. To a degassed solution of **8** (20 mg, 0.021 mmol), bromotrimethylsilylacetylene (5.6 mg, 0.031 mmol), [$PdCl_2(PPh_3)_2$] (0.5 mg, 3 mol%), and CuI (0.2 mg, 5 mol%) in dry THF (50 mL) was added TMEDA (0.1 mL), and the resulting mixture was stirred at 20 °C for 7 h under nitrogen pressure. After the solvent was evaporated, flash chromatography (SiO_2, hexane) yielded **13** together with a small amount of unreacted **8** (6.5 mg). Recrystallization from CS_2/pentane gave pure **13** (7.9 mg, 36% yield or 53% based on reacted starting material).

1,4-Bis{1,2-dihydro-61-[(triisopropylsilyl)ethynyl]-1,2-methanofullerene[60]-61-yl}buta-1,3-diyne (14). To **8** (70 mg, 0.075 mmol) and CuCl (600 mg, 6.0 mmol) in chlorobenzene (100 mL) was added TMEDA (0.85 mL, 5.5 mmol), and the mixture was vigorously stirred for 7 h in the presence of dry air. The resulting mixture was filtered through a pad of silica gel (toluene), and the solvent was evaporated. Flash chromatography (SiO_2, cyclohexane) followed by recrystallization from CS_2/pentane gave pure **14** (26 mg, 37% yield) as black crystals: m.p. > 270 °C). IR (KBr): 2933 (s), 2856 (s), 2167 (w), 1456 (m), 1422 (m), 878 (m), 678 (m), 522 (s). ^{1}H NMR (CS_2/C_6D_6 1:1, 200 MHz): 1.14 (s, 42 H). ^{13}C NMR (CS_2/C_6D_6 1:1, 125 MHz): 11.98, 19.18, 28.61, 69.72, 73.95, 75.31, 88.90, 97.20, 139.35, 139.55, 141.39, 141.53, 142.34, 142.39, 142.76, 143.08, 143.19, 143.27, 143.28, 143.31, 143.32, 144.28, 144.30, 144.90, 144.95, 144.97, 145.01, 145.24, 145.30, 145.39, 145.67, 145.68, 145.70 (2x), 145.71, 145.73, 145.76, 145.92. UV/Vis (CH_2Cl_2): 256 (110 000), 330 (37 200), 434 (2 300), 481 (1 600), 687 (200). MS (MALDI-TOF, negative ion mode): 720 (C_{60}^-), 1875 (M^-).

1-Hydro-2-[(trimethylsilyl)ethynyl]fullerene[60] (16). A solution of C_{60} (500 mg, 0.695 mmol) was treated with lithium trimethylsilylacetylide (10 mL of 0.2 M solution in THF, 2.0 mmol) under N_2. The purple solution slowly discolored, and a black precipitate formed. After 1 h TLC showed that most of the C_{60} had been consumed, so the reaction was quenched with acetic acid (0.5 mL). The product was isolated by flash chromatography (SiO_2, cyclohexane), and recrystallization from CS_2/Et_2O yielded **16** (324 mg, 58% yield) as black crystals: m.p. > 300 °C. IR (KBr): 2951 (w), 2921 (w), 2895 (w), 2850 (w), 2155 (w), 1510 (m), 1426 (m), 1246 (m), 1182 (m), 1094 (m), 854 (s), 839 (s), 757 (m), 631 (m), 526 (s). ^{1}H NMR ($CS_2/(CD_3)_2CO$ capillary), 200 MHz): 0.37 (s, 12 H), 6.92 (s, 1 H). ^{13}C NMR ($CS_2/(CD_3)_2CO$ capillary, 125 MHz): -0.04, 55.10, 61.82, 88.15, 107.33, 134.74, 135.73, 140.02, 140.04, 141.31, 141.36, 141.51, 141.70, 141.72, 141.75, 142.25, 142.29, 142.89, 144.17, 144.34, 145.01, 145.08, 145.17, 145.31, 145.36, 145.43, 145.87, 145.88, 146.04, 146.06, 146.30, 146.96, 147.22, 150.77, 150.98. UV/Vis (CH_2Cl_2): 256 (104 000), 306 (31 200), 327 (32 500), 404 (4 300), 431 (3 200), 701 (260). FAB-MS: 720 (100, C_{60}^+), 819 [50, $(M + H)^+$]. Anal. calc. for $C_{65}H_{10}Si$ (818.89): C 95.34, H 1.23; found: C 95.16, H 1.41.

1-Ethynyl-2-hydrofullerene[60] (18). A mixture of **16** (50 mg, 61 µmol) and K_2CO_3 (50 mg, 0.36 mmol) in THF/MeOH 1:1 (200 mL) was saturated with N_2 and refluxed for 3 h, then quenched with acetic acid (200 µL) and passed through a short plug of silica gel. Recrystallization from CS_2/pentane gave **18** (43 mg, 94% yield) as black crystals: m.p. > 300 °C. IR (KBr): 3289 (w), 1511 (m), 1428 (m), 1182 (m), 768 (w), 642 (m), 526 (s). ^1H NMR (CS_2/ $(CD_3)_2CO$ capillary, 500 MHz): 3.04 (s, 1 H), 6.98 (s, 1 H). ^{13}C NMR (CS_2/$(CD_3)_2CO$ capillary, 125 MHz): 71.82, 86.85, 135.77, 140.17, 140.23, 141.44, 141.49, 141.56, 141.85, 142.43, 142.84, 143.02, 144.27, 144.47, 145.14, 145.23, 145.30, 145.54, 146.01, 146.18, 146.21, 146.40, 150.63, 150.88. UV/Vis (CH_2Cl_2): 257 (30 000), 328 (11 600), 405 (4 700), 431 (3 200), 700 (300). MALDI-TOF-MS: 720 (100, C_{60}^+), 746 (31, M^+).

1-Benzyl-2-[(trimethylsilyl)ethynyl]fullerene[60] (19). A solution of C_{60} (200 mg, 0.278 mmol) in toluene (220 mL) was treated with lithium trimethylsilylacetylide (0.2 M, 3.0 ml; 0.6 mmol) and stirred for 1 h at 20 °C to give a black suspension. THF (50 ml) and benzyl bromide (200 µl, 1.68 mmol) were added, and the resulting green solution was stirred for at 20 °C for 2 h and subsequently heated to 60 °C for 2 h, by which time it had become brown. It was stirred overnight at 20 °C, then treated with acetic acid (100 µL), passed through a short plug (SiO_2, toluene) and evaporated to dryness. The product was isolated by flash column chromatography (SiO_2, cyclohexane) and recrystallized from CS_2/pentane to yield **19** (78 mg, 31% yield) as black crystals: m.p. > 300 °C. IR (KBr): 3028 (w), 2954 (w), 2143 (w), 1475 (m), 1422 (w), 1247 (m), 1116 (w), 1032 (w), 840 (s), 761 (m), 699 (m), 675 (s), 526 (s). ^1H NMR ($CDCl_3$/CS_2 1:1, 500 MHz): 0.48 (s, 9 H), 5.13 (s, 2 H), 7.24 (m, 1 H), 7.32 (t, J = 7.5, 2 H), 7.50 (d, J = 7.7, 2 H). ^{13}C NMR ($CDCl_3$/CS_2 1:1, 125 MHz): -0.06, 49.96, 60.79, 65.70, 91.89, 103.08, 127.03, 127.96, 131.73, 133.99, 134.42, 136.76, 138.56, 140.06, 141.05, 141.51, 141.55, 141.72, 141.91, 142.01, 142.38, 142.43, 142.89, 144.38, 144.39, 144.94, 145.13, 145.15, 145.19, 145.28, 145.68, 145.96, 146.07, 146.16, 146.23, 146.28, 147.41, 147.52, 153.39, 153.60. UV/Vis (CH_2Cl_2): 256 (110 000), 311 (37 300), 433 (3 700), 698 (360). FAB-MS: 720 (100, C_{60}^+), 909 [8%, $(M + H)^+$]. Anal. calc. for $C_{72}H_{16}Si$ (909.02): C 95.14, H 1.77; found: C 95.10, H 1.69.

1-Ethynyl-2-benzylfullerene[60] (20). a) From **19**. A solution of **19** (20 mg, 22 µmol) and K_2CO_3 (5 mg, 53 µmol) in THF/MeOH (35 mL, 4:1) was stirred at 20 °C for 2 h. Then the solution was passed through a short plug of silica gel to remove excess base and evaporated to dryness. The residue exhibited traces of low R_f impurities so it was passed through a second plug (SiO_2, CS_2) and recrystallized from CS_2/pentane to give **20** (13 mg, 71% yield) as black crystals: m.p. > 300 °C. IR (KBr): 3290 (w), 3277 (w), 3021 (w), 2916 (w), 1508 (m), 1429 (m), 1420 (m), 1263 (w), 1180 (w), 1107 (w), 1027 (w), 838 (w), 695 (m), 645 (m), 525 (s). ^1H NMR (CS_2/ $(CD_3)_2CO$ capillary, 500 MHz): 3.05 (s, 1 H), 5.03 (s, 2 H), 7.13 (t, J = 7.4, 1 H), 7.18 (t, J = 7.5, 2 H), 7.35 (d, J = 7.3, 2 H). ^{13}C NMR (CS_2/$(CD_3)_2CO$ capillary, 125 MHz): 50.45, 59.75, 65.73, 75.24, 82.71, 127.18, 128.09, 131.71, 134.10, 134.31, 136.35, 138.69, 140.07, 141.08, 141.53, 141.58, 141.67, 141.93, 142.04, 142.42, 142.46, 142.92, 144.36, 144.42, 144.74, 145.16, 145.21, 145.39, 145.65, 145.98, 146.10, 146.12, 146.24, 146.31, 147.40, 147.53, 153.04, 153.33. UV/Vis (CH_2Cl_2): 256 (119 000), 311 (39 000), 432 (3 800), 698 (350). FAB-MS: 720 (100, C_{60}^+), 745 [40, $(M - CH_2C_6H_5)^+$], 837 [30, $(M + H)^+$].

b) From **16**. A solution of **16** (80 mg, 0.098 mmol) in THF/methanol 5:1 (120 mL) was treated with K_2CO_3 (120 mg, 0.84 mmol) and benzyl bromide (100 µL, 0.84 mmol). The mixture was deoxygenated and refluxed for 2 h, whereupon the dark green solution slowly became pale brown. Flash chromatography (SiO_2, cyclohexane) and recrystallization from CS_2/pentane afforded pure **20** (28 mg, 34 % yield) as black crystals.

1-Hydroxymethyl-2-[(trimethylsilyl)ethynyl]fullerene[60] (25). To a solution of C_{60} (250 mg, 0.35 mmol) in toluene (250 mL) was added a solution of lithium trimethylsilylacetylide in THF (5.0 mL 0.2 M, 1.0 mmol), and the reaction mixture was stirred for 30 min at 20 °C. The resulting black suspension was cooled in an ice bath and formaldehyde gas (generated by depolymerization of paraformaldehyde at 170 °C) was passed over the solution until TLC analysis showed that, upon quenching with acetic acid, no more **16** was present. The solution was poured into a mixture of 0.1 N HCl (10 mL) and H_2O (100 mL), and the organic layer was washed with H_2O (50 mL) and brine (50 mL) and dried over $MgSO_4$. After evaporation of the solvent the product was purified from unreacted C_{60} by flash chromatography (SiO_2, cyclohexane/toluene 9:1 to 7:3) and recrystallized from CS_2/pentane to yield **25** (132 mg, 45% yield, 57% based on reacted C_{60}) as a brown solid: m.p. > 300 °C. IR (KBr): 2957 (w), 2922 (w), 2157 (w), 1429 (w), 1248 (m), 1213 (w), 1184 (w), 1142 (w), 1123 (w), 1114 (w), 1055 (m), 844 (s), 755 (s), 526 (s). ^1H NMR ($CDCl_3$, 200 MHz): 0.48 (s, 9 H), 4.20 (t, $J = 7.9$, 1 H), 5.64 (d, $J = 7.9$, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz): -0.20, 57.84, 69.81, 72.69, 90.43, 104.24, 134.75, 136.16, 140.23, 140.30, 141.54, 141.63, 141.96, 142.06, 142.19, 142.21, 142.66, 142.68, 144.62, 144.75, 145.12, 145.55, 145.57, 145.58, 145.64, 145.83, 145.92, 146.31, 146.35, 146.58, 146.63, 147.72, 147.91, 152.64, 152.91. UV/Vis (CH_2Cl_2): 256 (104 000), 310 (33 800), 432 (3 400), 696 (340). MALDI-TOF-MS: 720 (30, C_{60}^+), 818 [98, $(M - CH_2O)^+$], 848 (100, M^+). Anal. calc. for $C_{66}H_{12}OSi$ (848.92): C 93.38, H 1.42; found: C 93.54, H 1.23.

2-[(Trimethylsilyl)ethynyl]fullerene[60]-1-carboxaldehyde (27). To a solution of oxalyl chloride (25 μL, 0.295 mmol) in CH_2Cl_2 (3 mL) at -78 °C was slowly added a solution of Me_2SO (42 μL, 0.598 mmol) in CH_2Cl_2 (3 mL), and the mixture was stirred at -78 °C for 30 min. Then a solution of **25** (50 mg, 59 μmol) in CH_2Cl_2 (10 mL) was added, and the mixture was stirred for another 90 min at -78 °C. After adding NEt_3 (140 μL, 1.0 mmol) the solution was warmed to 20 °C over 15 min and subsequently poured into 0.1 N HCl (50 mL). CH_2Cl_2 (25 mL) was added, and the organic layer was washed with H_2O (2 x 10 mL) and brine (10 mL) and dried on Na_2SO_4. Evaporation of the solvent followed by recrystallization from CS_2/pentane afforded **27** (26 mg, 53% yield) as a brown powder: m.p. > 300 °C. IR (KBr): 2957 (m), 2922 (w), 2897 (w), 2834 (w), 2156 (m), 1730 (s), 1514 (s), 1506 (s), 1430 (m), 1248 (s), 1169 (m), 1126 (m), 1044 (m), 849 (s), 844 (s), 760 (m), 526 (s). ^1H NMR ($CDCl_3$, 200 MHz): 0.48 (s, 9 H), 11.3 (s, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz): -0.21, 57.12, 76.20 (characterized from measurement in CS_2), 94.79, 101.35, 134.75, 136.79, 140.25, 140.66, 141.63, 141.80, 141.84, 141.92, 142.17, 142.27, 142.75, 142.79, 144.57, 144.59, 144.96, 145.51, 145.57, 145.64, 145.66, 145.92, 146.34, 146.38, 146.57, 146.58, 147.49, 147.64, 147.83, 151.05, 192.38. UV/Vis (CH_2Cl_2): 255 (112 500), 319 (36 400), 431 (3 600), 691 (300). MALDI-TOF-MS (negative ion mode): 719 (26, C_{60}^-), 817 [93, $(M - CHO - H)^-$], 845 [100, $(M - H)^-$]. Anal. calc. for $C_{66}H_{10}OSi$ (846.89): C 93.60, H 1.19; found: C 93.68, H 1.02.

1-(*p*-Toluenesulfonylmethyl)-2-[(trimethylsilyl)ethynyl]fullerene[60] (28). A solution of **25** (70 mg, 82 μmol) and *p*-toluenesulfonyl chloride (200 mg, 0.82 mmol) in dry pyridine (5 mL) was stirred at 20 °C for 3 d. Then CH_2Cl_2 (25 mL) was added, and the solution was cooled to 0 °C. 2 N HCl (30 mL) was added, and the organic layer was washed successively with 0.1 N HCl (5 mL), H_2O (3 x 10 mL), and brine (10 mL), and dried on $MgSO_4$. After evaporation of the solvent the crude product was severely washed with pentane to remove excess of *p*-toluenesulfonyl chloride. Recrystallization from CS_2/pentane afforded pure **28** (33 mg, 40% yield) as black crystals: m.p. > 300 °C. IR (KBr): 2958 (w), 2922 (m), 2850 (w), 2157 (w), 1594 (m), 1376 (s), 1249 (w), 1189 (s), 1173 (s), 989 (m), 847 (s), 812 (m), 654 (s), 571 (s), 530 (s). ^1H NMR ($CDCl_3$, 200 MHz): 0.44 (s, 9 H), 2.45 (s, 3 H), 6.05 (s, 2 H), 7.35 (d, $J = 7.9$, 2 H), 7.93 (d, $J = 8.2$, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz): -0.09, 21.74, 58.35, 63.83, 74.94, 91.85, 101.18, 128.21, 129.99, 132.98, 134.14, 135.75, 139.65, 140.47, 141.49, 141.55, 141.73, 141.92, 142.25, 142.26, 142.71, 142.74, 144.62, 144.67, 144.95, 145.30, 145.52, 145.54, 145.73, 145.83, 146.28, 146.32, 146.41, 146.59, 146.63, 147.83, 147.88, 150.46, 152.24. UV/Vis (CH_2Cl_2): 256 (76 000), 312 (26 000), 431 (2 600), 693 (240). FAB-MS: 720 (100, C_{60}^+), 1002 (3, M^+).

X-Ray structure of 14: The X-ray measurements were made on an *Enraf-Nonius* CAD4 diffractometer equipped with graphite monochromator (Cu*Kα* radiation, $\lambda = 1.5418$ Å) and an *Enraf-Nonius* gas-stream low-temperature device. Black, plate-like single crystals, composed of **14** and solvent (in a ratio 1:2) were obtained by slow evaporation of a toluene solution. Crystal data at 100 K for $[(C_{148}H_{42}Si_2) \cdot 2(C_7H_8)]$, $M_r = 2060.2$; triclinic, space group $P\bar{1}$ (no. 2), $D_c = 1.51$ g cm^{-3}, $Z = 1$, $a = 10.024(2)$ Å, $b = 13.840(2)$ Å, $c = 17.126(2)$ Å, $\alpha = 75.32(1)^o$, $\beta = 87.51(1)^o$, $\gamma = 81.39(1)^o$, $V = 2272.4(5)$ Å^3. The structure was solved by direct methods and refined by full-matrix least-squares analysis (*SHELXTL PLUS*), using an isotropic extinction correction and an exponentially modified weight factor $r = 5$ Å^2. The co-crystallized solvents are slightly disordered. Final $R(F) = 0.047$, $wR(F) = 0.057$ for 771 variables and 5518 reflections with $I > 2\ \sigma(I)$ and $\theta < 76^o$ (heavy atoms anisotropic, H-atoms isotropic, whereby H-positions are based on stereochemical considerations). Additional experimental details of the crystal structure analysis are available on request from the *Cambridge Crystallographic Data Centre*, 12 Union Road, GB-Cambridge CB12 1EZ (UK), on quoting the full journal citation.

Table 1. Bond Lengths (Å) and Bond Angles [^{o}] of the Cyclopropane Ring and the Acetylenic Sub-units. Estimated Standard Deviations are ca. 0.004 Å and 0.3^o, Respectively.

C(1)-C(2)	1.575	C(1)-C(61)-C(2)	61.5
C(1)-C(61)	1.541	C(1)-C(2)-C(61)	59.3
C(2)-C(61)	1.537	C(2)-C(1)-C(61)	59.1
C(61)-C(62)	1.450	C(1)-C(61)-C(62)	115.9
C(62)-C(63)	1.213	C(1)-C(61)-C(73)	115.9
C(63)-Si(1)	1.849	C(2)-C(61)-C(62)	116.0
C(61)-C(73)	1.446	C(2)-C(61)-C(73)	117.0
C(73)-C74)	1.204	C(61)-C(62)-C(63)	172.7
C(74)-C(74a)	1.373	C(61)-C(73)-C(74)	178.1
		C(62)-C(63)-Si(1)	174.6
		C(62)-C(61)-C(73)	118.1
		C(73)-C(74)-C(74a)	178.7

Table 2. Selected Bond Angles [°] of the Bridged Pyracylene Sub-unit. Estimated Standard Deviations are ca. 0.3°.

C(2)-C(1)-C(9)	115.9	C(2)-C(3)-C(4)	122.6
C(2)-C(1)-C(6)	116.4	C(2)-C(3)-C(14)	108.2
C(6)-C(1)-C(9)	105.7	C(4)-C(3)-C(14)	119.6
C(1)-C(2)-C(3)	116.0	C(1)-C(9)-C(8)	107.9
C(1)-C(2)-C(12)	116.1	C(1)-C(9)-C(10)	123.4
C(3)-C(2)-C(12)	105.3	C(8)-C(9)-C(10)	119.3
C(1)-C(6)-C(5)	122.7	C(2)-C(12)-C(11)	122.8
C(1)-C(6)-C(7)	107.8	C(2)-C(12)-C(13)	108.3
C(5)-C(6)-C(7)	119.9	C(11)-C(12)-C(13)	119.4

Acknowledgements. We thank the Swiss National Science Foundation for financial support and a post-doctoral fellowship to P.T., the Engineering and Physical Sciences Research Council (U.K.) for a post-doctoral fellowship to H. L. A., and the European Communities for a post-doctoral fellowship (Human Capital and Mobility Program) to J.-F. N. We also thank J. Cuntze, E. Martinborough, M. Schreiber, and P. Wallimann for high-field ^{13}C NMR spectra.

5. REFERENCES AND NOTES

1 a) Diederich, F.; Rubin, Y. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1101-1123; b) Diederich, F. *Nature (London)*, **1994**, *369*, 199-207.

2 a) Anderson, H. L.; Faust, R.; Rubin, Y.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1366-1368; b) Anderson, H. L.; Boudon, C.; Diederich, F.; Gisselbrecht, J.-P.; Gross, M.; Seiler, P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1628-1632.

3 de Meijere, A.; Kozhushkov, S.; Puls, C.; Haumann, T.; Boese, R.; Cooney, M. J.; Scott, L. T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 869-871.

4 a) de Meijere, A.; Haumann, T.; Boese, R.; Puls, C.; Cooney, M. J.; Scott, L. T. *Chem. Eur. J.* **1995**, *1*, 124-131; b) Scott, L. T.; Cooney, M. J.; Otte, C.; Puls, C.; Haumann, T.; Boese, R.; Carroll, P. J.; Smith, A. B. III; de Meijere, A. *J. Am. Chem. Soc.* **1994**, *116*, 10275-10283.

5 An, Y. Z.; Rubin, Y.; Schaller, C. ; McElvany, S. W. *J. Org. Chem.* **1994**, *59*, 2927-2929.

6 Hauptmann, H. *Tetrahedron Lett.* **1974**, 3587-3588.

7 Bingel, C. *Chem. Ber.* **1993**, *126*, 1957-1959.

8 Schwesinger, R.; Schlemper, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1167-1169.

9 a) Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231-1250; b) Isaacs, L.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 2454-2464.

10 Anderson, H. L. *Inorg. Chem.* **1994**, *33*, 972-981.

11 a) Osterodt, J.; Nieger, M.; Vögtle, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1607-1608; b) Paulus, E. F.; Bingel, C. *Acta Cryst. C.* **1995**, *51*, 143-146.

12 Diederich, F.; Isaacs, L.; Philp, D. *J. Chem. Soc., Perkin Trans. 2* **1994**, 391-394.

13 Fedurco, M.; Costa, D. A.; Balch, A. L.; Fawcett, W. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 194-196.

14 Diederich, F.; Dietrich-Buchecker, C.; Nierengarten, J.-F.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1995**, 781-782.

15 a) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, Ö. *J. Am. Chem. Soc.* **1992**, *114*, 7300-7301; b) Belik, P.; Gügel, A.; Spickermann, J.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 78-80.

16 Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1993**, 813-824.

17 a) Hirsch, A.; Lamparth, I.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 437-438; b) Henderson, C. C.; Rohlfing, C. M.; Assink, R. A.; Cahill, P. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 786-788; c) Hirsch, A.; Lamparth, I.; Grösser, T.; Karfunkel, H. R. *J. Am. Chem. Soc.* **1994**, *116*, 9385-9386; d) Lamparth, I.; Maichle-Mössmer, C.; Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1995**, in press.

18 Isaacs, L.; Haldimann, R. F.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2339-2342.

19 a) Hawkins, J. M.; Meyer, A.; Solow, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 7499-7500; b) Herrmann, A.; Diederich, F.; Thilgen, C.; ter Meer, H.-U.; Müller, W. H. *Helv. Chim. Acta* **1994**, *77*, 1689-1706; c) Seiler, P.; Herrmann, A.; Diederich, F. *Helv. Chim. Acta* **1995**, *78*, 344-354.

20 For the construction of functionalized derivatives of carbon allotropes of type **1**, see: Isaacs, L.; Seiler, P.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1995**, in press.

21 Komatsu, K.; Murata, Y.; Takimoto, N.; Mori, S.; Sugita, N.; Wan, T. S. M. *J. Org. Chem.* **1994**, *59*, 6101-6102.

22 a) Hirsch, A.; Soi, A.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 766-768; b) Taylor, R.; Walton, D. R. M. *Nature (London)* **1993**, *363*, 685-693; c) Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1138-1141; d) Kampe, K.-D.; Egger, N.; Vogel, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1174-1176; e) Hirsch, A. *The Chemistry of the Fullerenes*, Thieme, Stuttgart, 1994, Chapt. 3, pp. 57-66; f) Kitagawa, T.; Tanaka, T.; Takata, Y.; Takeuchi, K. *J. Org. Chem.* **1995**, *60*, 1490-1491.

23 Fagan, P. J.; Krusic, P. J.; Evans, D. H.; Lerke, S. A.; Johnston, E. *J. Am. Chem. Soc.* **1992**, *114*, 9697-9699.

24 a) Varvoglis, A. *The Organic Chemistry of Polycoordinated Iodine*, VCH (New York), 1992; b) Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 274-285; c) Stang, P. J. in *Modern Acetylene Chemistry*, Stang, P. J.; Diederich, F. (Eds.), VCH, Weinheim, 1995, Chapt. 3.

25 a) Kende, A. S.; Fludzinski, P.; Hill, J. H.; Swenson, W.; Clardy, J. *J. Am. Chem. Soc.* **1984**, *106*, 3551-3562; b) Sauvêtre, R.; Normant, J. F. *Tetrahedron Lett.* **1982**, *23*, 4325-4328; c) Hopf, H.; Witulski, B. in *Modern Acetylene Chemistry*, Stang, P. J.; Diederich, F. (Eds.), VCH, Weinheim, 1995, Chapt. 2.

26 a) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769-3772; b) Posner, G. H.; Loomis, G. L.; Sawaya, H. S. *Tetrahedron Lett.* **1975**, 1373-1376; c) Anthony, J.; Boldi, A. M.; Rubin, Y.; Hobi, M.; Gramlich, V.; Knobler, C. B.; Seiler, P.; Diederich, F. *Helv. Chim. Acta*, **1995**, *78*, 13-45.

27 Kende, A. S.; Fludzinski, P. *Tetrahedron Lett.* **1982**, *23*, 2369-2372.

28 Bachi, M. D.; Bar-Ner, N.; Crittell, C. M.; Stang, P. J.; Williamson, B. L. *J. Org. Chem.* **1991**, *56*, 3912-3915.

29 Gilman, H.; Catlin, W. E. *Org. Synth.* **1932**, *1*, 188-190.

30 Zhang, X.; Romero, A.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 11024-11025.

31 Hauptmann, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 498-499; b) Hauptmann, H. *Tetrahedron Lett.* **1975**, 1931-1934.

32 Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627-630.

(*Received* 26 *May* 1995)