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Reactions of fullerenols $C_{60}(OH)_x$ ($x = 12, 18$) with trialkoxysilanes $(RO)_3Si(CH_2)_3X$ ($R = Me$, $X = Cl$; $R = Et$, $X = NH_2$)

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Abstract

Transesterification reactions of trialkoxysilanes $SiR(OR')_3$ [$R = (CH_2)_3Cl$, $R' = Me$; $R = (CH_2)_3NH_2$, $R' = Et$] with fullerenols $C_{60}(OH)_x$ ($x = 12, 18$) give different products containing totally or partially hydrolyzed $OSiR(OR')_2$, $O_2SiR(OR')$ and, possibly, O_3SiR attached species in a variable number. The yields with respect to the fullerenols are very high. © 1998 Elsevier Science S.A.

Keywords: C_{60}; Fullerenol; Trialkoxysilanes; Transesterification

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1. Introduction

Fullerenols $C_{60}(OH)_x$ are easily accessible by diverse preparative methods [1–8]. However, relatively few fullerenol derivatives have been described and they are limited to partially esterificated fullerenols with organic acids [1,2] and urethane-connected polyether dendritic polymers [9]. Here we report new transesterification reactions of functionalized propyl-trialkoxysilanes of the type $(RO)_3Si(CH_2)_3X$ ($R = Me$, $X = Cl$; $R = Et$, $X = NH_2$) with fullerenols $C_{60}(OH)_x$ ($x = 12$, 18). Potentially each SiOR group of a trialkoxysilane can give rise to a $C_{60}O–Si$ bond through a transesterification reaction, according to Eq. (1) and the remaining unreacted Si–OR bonds are sensible to hydrolysis.

$$R–O–Si + R'–OH \rightarrow R'–O–Si + R–OH \qquad (1)$$

2. Results and discussion

The fullerenols here used were synthesized as described by Chiang et al. [5] by hydrolysis of their polycyclosulfated fullerene precursors prepared by treatment of C_{60} with fuming sulfuric acid (33% SO_3) at 65°C for 3 days under N_2. In these conditions the fullerenol $C_{60}(OH)_{12}$ (**1**) was formed. It is to be noted that the composition of the fullerenol is strongly dependent on the SO_3 concentration of the fuming sulfuric acid. So a polycyclosulfated fullerene prepared from a mixture of C_{60} (0.5 g), fuming sulfuric acid (65% SO_3, 5 ml) and H_2SO_4 (98%, 3 ml), heated for 24 h at 65°C under N_2 and subsequently hydrolyzed, yields a fullerenol of composition $C_{60}(OH)_{18}$ (**2**).

Both fullerenols are probably not single compounds. Two from fifteen selected possible isomers have been predicted as the most likely structures for $C_{60}(OH)_{12}$ in a recent theoretical study based on considerations of thermodynamical stabilities and the cyclosulfation and hydrolysis mechanisms [10]. Although the 6,6-addition is the most favoured in the formation of polycyclosulfates, the most probable sites for the attack of two water molecules are those located on adjacent carbons to the 6,6-junctions occupied by SO_4 groups. The most stable isomer (*A*, S_6 symmetry) (Fig. 1) predicted from thermodynamical considerations for $C_{60}(OH)_{12}$ contains all OH groups occupying *para* or *metha* positions of a chain of adjacent hexagons on the surface of the fullerene cage. On the other hand, the most probable isomer predicted from hydrolysis reaction mechanism (*B*, also with S_6 symmetry) contains two groups of six hydroxyls, three of each group occupying 1,3,5 positions around a hexagon and the three remaining occupying the *trans* positions of all three adjacent hexagons, the central hexagons of both groups being centred at the

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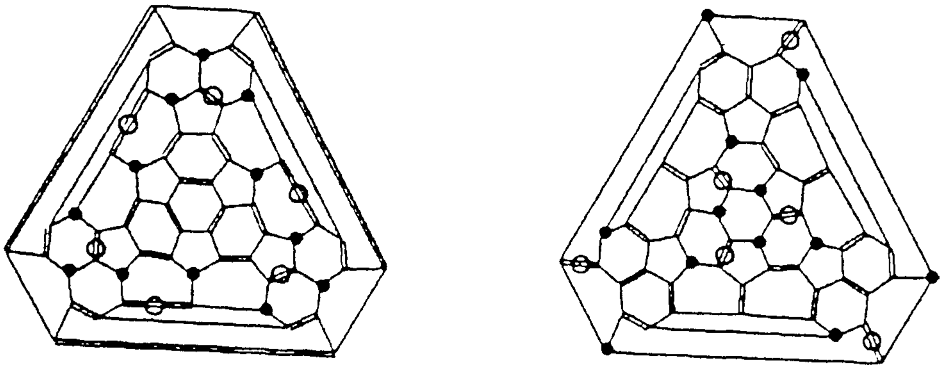

$C_{60}(OH)_{12}$ - *A* $C_{60}(OH)_{12}$ - *B*

Fig. 1. Schlegel diagrams for the most favoured isomers, *A* (S_6) and *B* (S_6), of fullerenol $C_{60}(OH)_{12}$ [10].

opposite sides of the principal symmetry axis. Although a similar study about the most favoured from the possible isomers of $C_{60}(OH)_{18}$ has been not performed, it is highly probable the presence of groups of two (*metha* or *para*) or three 1,3,5 hydroxyls on a number of hexagons of the fullerene cage.

$C_{60}(OH)_{12}$ reacts with $(MeO)_3Si(CH_2)_3Cl$ in a molar ratio 1/16.5, in refluxing THF for 24 h under N_2, to yield a brown suspension, from which a dark brown solid (**3**) was separated as the majoritary product. A second reddish-brown solid (**4**) was isolated from solution after removal of the solvent and washing with diethyl ether. Solid **3** shows an IR spectrum very similar to that of the starting fullerenol, but **4** shows relatively intense IR bands of the attached organic groups. However ^1H NMR and solid-state ^{13}C NMR spectra of **3** and **4** show signals characteristic of the attached organic groups, from which we conclude that they are reaction products containing a different number of organic substituents. **3** is presumably a product containing a single substituent, to which can be assigned the formula $C_{60}[OSi(OMe)(OH)(CH_2)_3Cl](OH)_{11}$. There are four possible isomers for a monosubstituted derivative from the more stable isomer *A* of $C_{60}(OH)_{12}$ and only two from the *B* isomer. Product **3** can be a single isomer or a mixture of isomers of similar stability. This product is very insoluble in THF and its original composition should be $C_{60}[OSi(OMe)_2(CH_2)_3Cl](OH)_{11}$. Partial or total hydrolysis can take place during manipulation for analysis or spectral characterization. Because of its low solubility, product **3** seems to be not an intermediate in the formation of **4**, which is still the minoritary product after 3 days of reaction. It is to be noted that the yields in products **3** and **4** after 1 or 3 days of reaction are approximately the same, the analytical and spectral data of products **3** and **4** of both reactions being reproducible. **4** results probably from the simultaneous attack of two or more silane molecules on the same molecule of fullerenol, giving rise to more soluble species. The analytical data show a low H content, which renders probable the presence of $RSiO_2$ or $RSiO_3$ groups bonded to two *metha* or *para* carbons or to three 1,3,5 carbons, respectively, of C_{60} hexagons of the most favoured fullerenol isomers [10]. All these three bonding modes are geometrically possible and transformation of attached $RSiO(OR')_2$ groups ($R' = Me$, H) into $RSiO_2(OR')$ or $RSiO_3$ could take place during elimination of solvent. The formula $C_{60}[O_2Si(OH)(CH_2)_3Cl]_2[OSi(OMe)(OH)(CH_2)_3Cl](OH)_7$ is assignable to **4** for derivatives of both *A* and *B* most favoured isomers of $C_{60}(OH)_{12}$ and the formula $C_{60}[O_3Si(CH_2)_3Cl][O_2Si(OMe)(CH_2)_3Cl]_3(OH)_3$ is assignable only to a compound **4** derived from the isomer *B*. This last formula could explain the relatively low number of addends in product **4** in spite of the great excess of trialkoxysilane. A quantitative study of reaction leads to conclude that fullerenol $C_{60}(OH)_{12}$ converts into products **3** and **4** in a high rate (90–95%) in the reaction with excess of $(MeO)_3Si(CH_2)_3Cl$.

A similar reaction in THF of $C_{60}(OH)_{18}$ and $(MeO)_3Si(CH_2)_3Cl$, in a molar ratio 1/13.34, yields a red-brown solution, from which a brown solid (**5**) was isolated after removal of the solvent. IR and ^{1}HNMR spectra are very similar with those of compound **4**, except in the higher intensities of the IR bands and ^{1}HNMR signals of the attached organic groups, as corresponding to a total substitution of OH groups in the starting fullerenol **2**. Analytical data are in a good agreement with the formula $C_{60}[O_2Si(OH)(CH_2)_3Cl]_6[OSi(OMe)_2(CH_2)_3Cl]_6$. In this case fullerenol **2** reacts also almost quantitatively (90.3%) to yield the product **5**. Other formulae such as $C_{60}[O_2Si(OMe)(CH_2)_3Cl]_7[OSi(OH)_2(CH_2)_3Cl]_4$ are also possible.

The reactions of both fullerenols with triethoxysilylpropylamine yield products with six attached organic groups. These products are very sensitive to moisture and their original composition is difficult to be determined. Hydrolysis of Si–OEt bonds and hydration of the resulting strong polar products, due to the presence of OH and NH groups, give rise to different derivatives and it is possible that the samples of the same product used for the different characterization methods result hydrolyzed and hydrated in a different extent during manipulation. Reaction of fullerenol $C_{60}(OH)_{12}$ and $(EtO)_3Si(CH_2)_3NH_2$ in a molar ratio 1/15.5, in the conditions described above, yields a brown precipitate of a product (**6**), with a high number of substituents as deduced from the relatively high intensities of the IR bands of the attached organic groups, specially those corresponding to the O–Si bonds. It is to be noted also the presence of a broad and intense IR band in the OH + NH stretching region, which can be partially due to the presence of water molecules. Only signals of ethanol are observed in the ^1H NMR spectrum in DMSO of this likely partially hydrolyzed sample because of total hydrolysis with the solvent moisture, to give an insoluble product. Solid-state ^{13}C NMR spectrum evidences also the absence of ethyl groups. This spectrum shows the characteristic signals expected for the sp^2 and sp^3 carbons of the fullerene cage and for those of the attached $OSi(OH)_2(CH_2)_3N$ groups. Additional N–C bonds with fullerene carbons, similar to those of the $[C_{60}]$-*N*,*N*-dimethyl-ethylenediamine adduct [11] are also possible. These carbons show a ^{13}C NMR signal at 78 ppm, which could be included in the sp^3 carbons signal at 78.45 ppm appearing in this spectrum. Analytical data seem to correspond to a totally hydrolyzed and hydrated product of composition $C_{60}[OSi(OH)_2(CH_2)_3NH]_6(OH)_6.10H_2O$. The high number of polar hydroxyls and NH groups renders plausible the presence of strong hydrogen bonding with water molecules. In this case fullerenol **1** converts also into **6** in a high yield (98%).

The reaction in THF of $C_{60}(OH)_{18}$ and $(EtO)_3Si(CH_2)_3NH_2$, in a molar ratio 1/13.2, in the conditions described above, leads to a brown product (**7**), which freshly obtained is soluble enough in benzene to give a good ^{1}HNMR spectrum in this solvent. The integration of the signals reveals a molar ratio 1/1 between OEt groups and CH_2–CH_2–CH_2 chains and the presence of two different methylene and methyl signals for EtO groups seems to indicate the presence of two different ethoxy groups in a partially hydrolyzed product, with a composition near to $C_{60}[OSi(OH)_2(CH_2)_3NH]_3[OSi(OEt)_2(CH_2)_3NH]_3(OH)_{12}$. No signals for NH or CH protons resulting from addition of NH_2 groups to fullerene double bonds nor for NH_2 protons were observed. ^{1}HNMR spectrum in DMSO shows only intense EtOH signals, due probably to a total hydrolysis of the sample and formation of an insoluble product. Analytical results of a sample careful handled in absence of moisture correspond to the composition $C_{60}[O_2Si(OH)(CH_2)_3NH][OSi(OH)_2(CH_2)_3NH]_2[OSi(OEt)_2(CH_2)_3NH]_3(OH)_{11}$. The analysis of a sample of the same product after a short exposure to air, without evacuation, corresponds to a totally hydrolyzed and hydrated product of composition $C_{60}[OSi(OH)_2(CH_2)_3NH]_6(OH)_{12} \cdot 5EtOH \cdot 5H_2O$, in which the ethanol formed was partially retained. The ^1H NMR spectrum and composition of **7** seem to indicate that the hydrolysis of the original product, probably of composition near to $C_{60}[OSi(OEt)_2(CH_2)_3NH]_6(OH)_{12}$, break preferentially Si–OEt bonds of the same attached group in the successive hydrolysis steps. The partial hydrolysis of the original product could take place during the manipulations to isolate the product, after elimination of solvent. The totally hydrolyzed products seem to be very hygroscopic, as deduced from analytical data of the same sample after a short exposure to air. This can also explain the analytical data for the totally hydrolyzed product **6**. The conversion of fullerenol **2** into product **7** is quantitative.

In general, both $C_{60}(OH)_{12}$ and $C_{60}(OH)_{18}$ fullerenols react almost quantitatively with the trialkoxysilanes here used in a varying manner and extent to give products containing a variable number of substituents. In the reactions with $(MeO)_3Si(CH_2)_3Cl$ products containing addends bonded through two or three oxygens to fullerene carbons, such as **4** and **5**, are formed. However the reactions with $(EtO)_3Si(CH_2)_3NH_2$ lead to products containing six addends, which seem to be preferentially bonded only through one oxygen to the fullerene carbons, remaining unreacted a relatively high number of OH groups of the original fullerenols. This can be due to the different steric hindrance of OMe and OEt groups and/or to the possible formation of additional bonds through the NH_2 groups.

3. Experimental

C_{60} was separated from refined mixed fullerene (MER, about 80% C_{60}) by flash chromatography as previously described [12]. All reactions were carried out under an atmosphere of dry N_2 free of oxygen. Solvents were purified and dried by standard methods. Elemental analyses were performed at the ICMM (CSIC). IR spectra were recorded with a Pye Unicam SP-3-300- or with a Nicolet 20 SXC FT–IR spectrophotometer, using KBr disks. NMR spectra in solution were recorded on a Varian Gemini 200. High resolution ^{13}C MAS or CP/MAS NMR spectra of powdered samples, in some cases also with a Toss sequence, in order to eliminate the spinning side bands, were recorded at 100.63 MHz, 6 μs 90° pulse width, 2 ms contact time and 5–10 recycle delay, using a Bruker MSL 400 spectrometer equipped with an FT unit. The spinning frequency at the magic angle (54°44′) was 4 KHz.

3.1. Preparation of polycyclosulfated fullerene

A mixture of C_{60} (1.00 g), H_2SO_4 (20% SO_3) (10 ml) and H_2SO_4 (60% SO_3) (5 ml) was stirred at 60°C for 3 days under N_2 to give a suspension of an orange solid. This suspension was added dropwise into diethyl ether (200 ml distilled over CaH_2) cooled in an ice bath, under vigorous stirring. After centrifugation, the orange solid was washed three times with diethyl ether and dried in air (1.76 g, 69%). Anal. Found: C, 41.99; H, 1.35; S, 17.37. Calc. for $C_{60}(SO_4)_6 \cdot 4H_2O \cdot 4H_2SO_4 \cdot Et_2O$, $C_{64}H_{26}O_{45}S_{10}$: C, 41.88; H, 1.43; S, 17.47. IR (cm^{-1}): 3428s,br, 2918vw, 1622w, 1424s, 1232vs, 1166sh, 1053m, 1000m, 976m, 950m, 850m, 834m, 820m, 638w, 590m, 524vw.

3.2. Preparation of fullerenols

*3.2.1. $C_{60}(OH)_{12}$ (**1**)*

A 1752 mg of polycyclosulfated fullerene (0.95 mmol) was heated with water (35 ml) at 85°C for 20 h under stirring to yield a suspension of a brownish red solid, which was centrifuged, washed three times with water (20 ml each) and dried at 110°C overnight in an oven, to yield 870 mg of a brownish-red powder (98.6%) of **1**. Anal. Found: C, 76.83; H, 1.37, Calc. for $C_{60}(OH)_{12}$ $0.5H_2O$, $C_{60}H_{13}O_{12.5}$ calc.: C, 77.18, H, 1.40. IR (cm^{-1}): 3392s,br, 1616m, 1380w,br 1043s (COH), 514w,br. Solid-state ^{13}CNMR (CP-MAS/TOSS) δ 145.11 (br, 155–135, sp^2 carbons), 80.75 (br, 84–67, sp^3 carbons).

*3.2.2. $C_{60}(OH)_{18}$ (**2**)*

A polycyclosulfated fullerene prepared from a mixture of C_{60} (0.5 g), fuming sulfuric acid (65% SO_3, 5 ml) and H_2SO_4 (98%, 3 ml), heated for 24 h at 65°C under N_2, was hydrolyzed and isolated as above described to yield **2** (499 mg, 70%) as a reddish-brown powder. Anal. Found: C, 70.55; H, 1.64. Calc. for $C_{60}H_{18}O_{18}$: C, 70.19; H, 1.76.

3.3. Reaction of $C_{60}(OH)_{12}$ with $Si(OMe)_3(CH_2)_3Cl$

A mixture of 100 mg of **1** (0.107 mmol) and 350 mg of $Si(OMe)_3(CH_2)_3Cl$ (1.76 mmol) was sonicated in dry THF (25 ml) for 15 min and refluxed for 24 h under an N_2 atmosphere. A brown solid appears which was centrifuged, washed two times with Et_2O and dried under vacuum (**3**, 71 mg, 61.7% referred to fullerenol). The remaining solution was evaporated and the reddish-brown residue was washed several times with Et_2O and dried under vacuum (**4**, 48 mg, 33.6% referred to fullerenol).

*3.3.1. $C_{60}[OSi(OMe)(OH)(CH_2)_3Cl](OH)_{11}$ (**3**)*

IR (cm^{-1}): 3398vs,br, 32914w, 2848w, 1615m, 1380m,br, 1050s, 536w. Except the band at 1050 cm^{-1}, which appears slightly displaced towards the higher frequencies and shows also a higher intensity than the band at 1043 cm^{-1} of $C_{60}(OH)_{12}$, these bands are coincident with those of the starting polyhydroxylated fullerene **1**. ^{1}HNMR (DMSO, 40°C, 200 MHz) δ 3.67–3.47 (m, 2H, CH_2), 1.88–1.68 (m, 2H, CH_2), 0.90–0.60 (m, 2H, CH_2) (this spectrum corresponds to a totally hydrolyzed sample; signals of OH groups are obscured by an intense signal of water in DMSO, centred at 3.35 ppm). Solid-state ^{13}CNMR (CP-MAS/TOSS) spectrum shows a broad signal with peaks at δ 155.20, 147.29 (max.), 142.26, 139.51, 136.67, 134.10 and 131.30 ppm, corresponding to the sp^2 carbons of the fullerene cage. The remaining sp^3 fullerene carbons appear included in a second broad signal centred at δ 80.45 ppm, with shoulders at δ 87.32, 75.00 and 71.52, which can be assigned to carbons bonded to OH and OSi groups. Signals at 68.43, 48.00, 26.25 and 11.21 ppm can be assigned to OMe, and methylene groups of the $ClCH_2–CH_2–CH_2Si$ chain, respectively, in this order. Anal. Found: C, 70.97; H, 1.82. Calc. for $C_{60}[OSi(OMe)(OH)(CH_2)_3Cl](OH)_{11}$, $C_{64}H_{21}ClO_{14}Si$: C, 71.35; H, 1.96%. Calc. for $C_{60}[OSi(OH)_2(CH_2)_3Cl](OH)_{11}$, $C_{63}H_{19}ClO_{14}Si$: C, 71.16; H, 1.80.

*3.3.2. $C_{60}[O_2Si(OH)(CH_2)_3Cl]_2[OSi(OMe)(OH)(CH_2)_3Cl](OH)_7$ or $C_{60}[O_3Si(CH_2)_3Cl][O_2Si(OMe)(CH_2)_3Cl]_3(OH)_3$ (**4**)*

IR (cm^{-1}): 3354s,br, 2944m, 2850vw, 1616w, 1432w, 1402w, 1312m, 1263m, 1230m, 1185sh, 1160sh, 1110vs (SiO), 1060vs (COH), 912m, 896m, 790m,br, 690m, 640w, 463m,br, 382w. ^{1}HNMR (DMSO, 40°C, 200 MHz) δ 3.70–3.40 (m, CH_2 + Me), 1.90–1.66 (m, CH_2), 0.90–0.60 (m, CH_2) (this spectrum corresponds to a totally hydrolyzed sample; signals of OH groups and residual MeOH are obscured by an intense signal of water in DMSO, centred at 3.35 ppm). Solid-state ^{13}C NMR (CP-MAS/TOSS) spectrum shows a broad signal with peaks at δ 157.10, 149.16 (max.), 147.05v (max.) 144.78, 142.79, 139.89 and 135.20, corresponding to the sp^2 carbons of the C_{60} cage. A second broad signal with peaks at δ 87.67, 81.42 (max.), 79.35 (max.), 75.92, 72.30 and 71.61 includes the sp^3 C_{60} carbons bonded to unreacted OH and to the OSi groups. Signals at 68.29, 47.75, 26.52 and 10.44 can be assigned to MeO and methylene groups of the $ClCH_2–CH_2–CH_2Si$ chain, respectively, in this order. Anal. Found C, 63.31; H, 2.24. Calc. for $C_{60}[O_2Si(OH)(CH_2)_3Cl]_2[OSi(OMe)(OH)(CH_2)_3Cl](OH)_7$, $C_{70}H_{31}Cl_3O_{16}Si_3$: C, 63.76; H, 2.37. Calc. for $C_{60}[O_3Si(CH_2)_3Cl][O_2Si(OMe)(CH_2)_3Cl]_3(OH)_3$, $C_{75}H_{36}Cl_4O_{15}Si_4$ (1431.26): C, 62.94; H, 2.54.

3.4. Reaction of $C_{60}(OH)_{18}$ with $Si(OMe)_3(CH_2)_3Cl$

3.4.1. $C_{60}[O_2Si(OH)(CH_2)_3Cl]_6[OSi(OMe)_2(CH_2)_3Cl]_6$ (**5**)

A mixture of 30 mg of **2** (0.029 mmol) and 77 mg of $Si(OMe)_3(CH_2)_3Cl$ (0.387 mmol) was sonicated in dry THF (10 ml) for 15 min and refluxed for 24 h under an N_2 atmosphere. The resulting reddish brown solution was evaporated and the residue (**5**) was washed several times with Et_2O and dried under vacuum (72 mg, 90.3% referred to fullerenol). IR (cm^{-1}): 3406m,br, 2944s, 2850m, 1616w, 1436m, 1408w, 1347w, 1310m, 1268m, 1236m, 1185sh, 1160sh, 1126vs (SiO), 1065vs (COH), 1000vs, 909m, 860mw 798m,br, 692s, 645w, 468m,br, 385m. ^{1}HNMR (DMSO, 40°C, 200 MHz) δ 3.59 (m, br, CH_2), 1.82 (m, br, CH_2), 0.76(m, br, CH_2) (this spectrum corresponds to a hydrolyzed sample; signals of OH groups and residual MeOH are obscured by an intense signal of water in DMSO, centred at 3.35 ppm). Anal. Found: C, 47.24; H, 3.74. Calc. for $C_{60}[O_2Si(OH)(CH_2)_3Cl]_6[OSi(OMe)_2(CH_2)_3Cl]_6$, $C_{108}H_{114}Cl_{12}O_{36}Si_{12}$: C, 47.16; H, 4.18. Calc. for $C_{60}[O_2Si(OMe)(CH_2)_3Cl]_7[OSi(OH)_2(CH_2)_3Cl]_4$, $C_{100}H_{95}Cl_{11}O_{33}Si_{11}$: C, 47.59; H, 3.79.

3.5. Reaction of $C_{60}(OH)_{12}$ with $Si(OEt)_3(CH_2)_3NH_2$

3.5.1. $C_{60}[OSi(OH)_2(CH_2)_3NH]_6(OH)_6 \cdot 10H_2O$ (**6**)

1 (100 mg, 0.107 mmol) and $Si(OEt)_3(CH_2)_3NH_2$ 367 mg, 1.66 mmol) were sonicated for 15 min in dry THF (25 ml) and refluxed for 24 h under N_2. The brown solid resulting (**6**) was filtered off, washed two times with Et_2O and dried under vacuum (190 mg). IR (cm^{-1}): 3392s,br, 3267sh, 2958sh, 2922m, 1622m, 1556m, 1430w, 1380w, 1329mw, 1182sh, 1086vvs, 1050vs, 910mw, 756mw, 690mw, 456m,br. Solid-state ^{13}C NMR (CP-MAS/TOSS) spectrum shows two broad signals corresponding to the carbons of the fullerene cage. The sp^2 carbons appears as a broad signal with peaks at δ 162.54, 152.00, 150.10, 147.15, 143.61 (max.), 140.05 (max.), 137.00, 135.44 and 132.15. The second broad signal, with peaks at δ 80.50, 78.45 (max.), 75.00 and 71.51, can be assigned to sp^3 carbons of the fullerene cage bonded to OSi groups. The well defined signals at 67.90, 26.04 and 10.02 ppm are assigned to the methylene groups of the $NCH_2CH_2CH_2Si$ chain, in this order. Anal. Found: C, 51.56; H, 4.20; N, 4.67. Calc. for $C_{60}[OSi(OH)_2(CH_2)_3NH]_6(OH)_6 \cdot 10H_2O$, $C_{78}H_{80}N_6O_{34}Si_6$: C, 51.64; H, 4.44; N, 4.65.

3.6. Reaction of $C_{60}(OH)_{18}$ with $Si(OEt)_3(CH_2)_3NH_2$

3.6.1. $C_{60}[O_2Si(OH)(CH_2)_3NH][OSi(OH)_2(CH_2)_3NH]_2[OSi(OEt)_2(CH_2)_3NH]_3(OH)_{11}$ (**7**)

A reaction similar to that earlier described from **2** (30 mg, 0.029 mmol) and $Si(OEt)_3(CH_2)_3NH_2$ (85 mg, 0.384 mmol) in dry and deaerated THF (10 ml) yields a brown solution, which after evaporation of solvent gives rise to a brown solid **7**, which was filtered off, washed two times with Et_2O and dried under vacuum (54 mg, 99%). IR (cm^{-1}): 3392s,br, 3267sh, 2960m, 2922m, 2880sh, 1622m, 1556m, 1476w, 1440w, 1425vw, 1388m, 1332sh, 1329sh, 1182sh, 1109vs (SiO), 1076sh, 1043vs (COH), 925m, 772mw, 690w, 448m,br. ^{1}HNMR (C_6D_6, 200 MHz) δ 3.59 (m, 2H, CH_2), 3.31(quartet, 1 H, OCH_2), 3.27 (quartet, 1 H, OCH_2), 1.40 (m, 2H, NCH_2), 0.94 (t, 1.5 H, Me), 0.93 (t, 1.5 H, Me), 0.40 (s, br, 5 H, OH + $SiCH_2$). Anal. Found: C, 57.38; H, 4.36; N, 4.49. Calc. for $C_{60}[O_2Si(OH)(CH_2)_3NH][OSi(OH)_2(CH_2)_3NH]_2[OSi(OEt)_2(CH_2)_3NH]_3(OH)_{11}$, $C_{90}H_{88}N_6O_{29}Si_6$: C, 57.31; H, 4.70; N, 4.45. Calc. for $C_{60}[OSi(OH)_2(CH_2)_3NH]_3[OSi(OEt)_2(CH_2)_3NH]_3(OH)_{12}$, $C_{90}H_{88}N_6O_{29}Si_6$: C, 56.77; H, 4.76; N, 4.41.

The same product after a short exposure to air, without evacuation: Anal. Found: C, 51.33; H, 4.98; N, 4.11. Calc. for $C_{60}[OSi(OH)_2(CH_2)_3NH]_6(OH)_{12}$. 5EtOH. $5H_2O$, $C_{88}H_{106}N_6O_{40}Si_6$:C, 51.540; H, 5.19; N, 4.09.

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