

Synthesis of Isomerically Pure Organodihydrofullerenes

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Controlled two-step nucleophilic hydroalkylations, hydroarylations as well as hydrostannylation of fullerene-60 (**1**) and fullerene-70 (**2**) lead to defined organodihydrofullerenes $C_{60}HR$ and $C_{70}HR$. NMR investigations show that only one isomer of each organodihydrofullerene with C_s symmetry is

formed. In all cases the addition takes place at a double bond separating two six-membered rings of the fullerene core. In this way a variety of organodihydrofullerenes also carrying functional groups have been synthesized.

The spherical all-carbon I_h molecule fullerene-60 (C_{60}) consists of 12 isolated pentagons and 20 hexagons. Structural data^[1] and calculations^[2] demonstrate that the bonds between two hexagons (6–6 bonds) exhibit double-bond character. The bonds between the pentagons and hexagons (5–6 bonds) with single-bond character are significantly longer, also showing a much lower electron density. Therefore, fullerene-60 can be considered a sphere built up of fused [5]radialene and cyclohexatriene units. This structural argument is supported by its chemical reactivity. One-step additions to C_{60} , namely the addition of osmium tetroxide^[3], transition-metal complexes^[4] or 1,3-dipoles^[5], exclusively take place at the 6–6 bonds. The other important chemical property of C_{60} (**1**) is its high electrophilicity^[6] and affinity towards radicals^[7]. Due to the polyfunctionality (thirty 6–6 bonds), an uncontrolled reaction leads to a huge number of different addition products which are impossible to isolate. Only few examples for the preparation of isomerically pure single compounds are known^[3–5,8–11]. Recently^[9], we have shown that it is possible to control even two-step nucleophilic additions to a 6–6 bond and to isolate the isomerically pure organodihydrofullerenes 1-*tert*-butyl- and 1-ethyl-1,9-dihydrofullerene-60^[12] (**5b** and **5c**). Thereby **1** was titrated with *tert*-butyllithium or ethylmagnesium bromide and subsequently protonated under HPLC control. This method opens up the access to a variety of functionalized organodihydrofullerenes which for example can serve as precursors for further reactions. Independently, **5b** was prepared by Fagan et al. using another procedure^[13]. The experi-

mental findings^[9,13] that two-step additions to fullerene-60 lead to the 1,9-isomers are confirmed by the calculation of their stability relative to other possible regioisomers^[9,14].

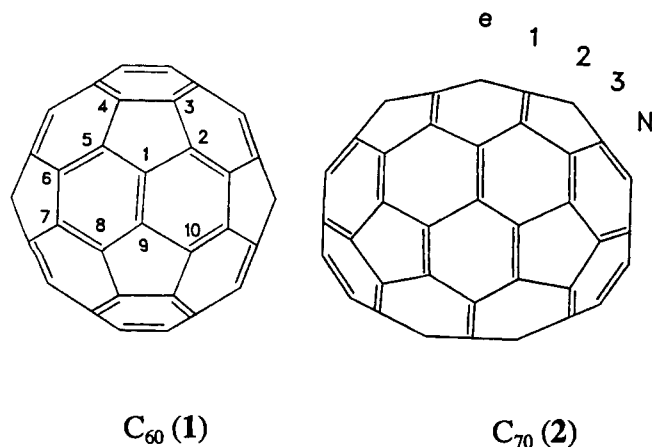
Fullerene-70 (**2**) with D_{5h} symmetry consists of 5 different sets of C atoms, which have been assigned as N, 3, 2, 1, e^[15]. The closest geometrical similarity to fullerene-60 is given at the pole areas of C_{70} . Although the regiochemistry for additions to the fullerene core seems to be more complicated in the case of C_{70} , predictions on nucleophilic additions indicate, that among the large number of possible isomers only a few are energetically favored^[15].

In this paper we show that the titration method^[9] can generally be used for the hydroalkylation and hydroarylation of fullerene-60. Also the addition of radicals can be controlled quantitatively by HPLC. In this way we prepared a variety of isomerically pure 1,9-adducts of **1** and determined their spectroscopic properties. For the first time we performed the additions of nucleophiles to fullerene-70 (**2**) by using our titration method and showed that also in this case single regioisomers with C_s symmetry are formed.

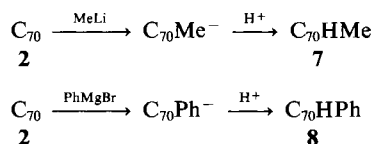
Results and Discussion

Synthesis of Organodihydrofullerenes 5–8

C_{60} (**1**) and C_{70} (**2**) were treated with various nucleophiles in benzene because besides carbon disulfide mainly aromatic solvents guarantee a sufficient solubility. The nucleophile addition, carried out stepwise, leads to a dark brown precipitate of the fullerenes **3**, **4** and $C_{70}R^-$, which upon rapid stirring is suspended homogeneously. Because of their high reactivity towards **1** and **2** the organolithium reagents were added in small amounts (0.2 equiv. each). After 1.2 equiv. (Table 1), the addition was stopped because the formation of higher adducts ($C_{60}R_2Li_2$, $C_{60}R_3Li_3$ etc.) set in. Use of milder Grignard compounds as nucleophiles necessitated 5–27 equiv. to obtain the maximum yield of the organodihydrofullerenes **5c–h**, **8** (Table 1). The titration was stopped at this point after which the amount of monoaddition products decreases again. The product formation as well as the consumption of **1** and **2** were followed quanti-



tatively by HPLC. Samples of the intermediates **3**, **4** or $C_{70}R^-$ were removed from the reaction mixtures, protonated with 0.01 M hydrogen chloride in methanol and diluted with hexane to a volume of 10 ml. The HPLC peaks can unambiguously be attributed to the corresponding compounds due to their UV/Vis spectra by simultaneously recorded diode-array scans. After the titration, the reaction mixture was quenched with 0.01 M hydrogen chloride in methanol to give compounds **5**, **7** and **8**. All monoaddition products synthesized are less soluble in organic solvents than C_{60} (**1**) and C_{70} (**2**) themselves. The purification of compounds **5**–**8** can either be done by preparative HPLC [C18, $CHCl_3/CH_3CN$ (60:40)] or by flash chromatography on silica gel. The main problem of the latter method is that usually a large amount (80–95%) of hexane has to be used as the mobile phase in order to obtain a sufficient separation. The low solubility of the organofullerenes in hexane allows the separation of only small quantities (<5 mg) of crude product in one run. All organodihydrofullerenes isolated show a purity of >98% (HPLC). During a period of three weeks, hexane solutions of the purified organodihydrofullerenes were repeatedly checked with HPLC. No decomposition was detected.

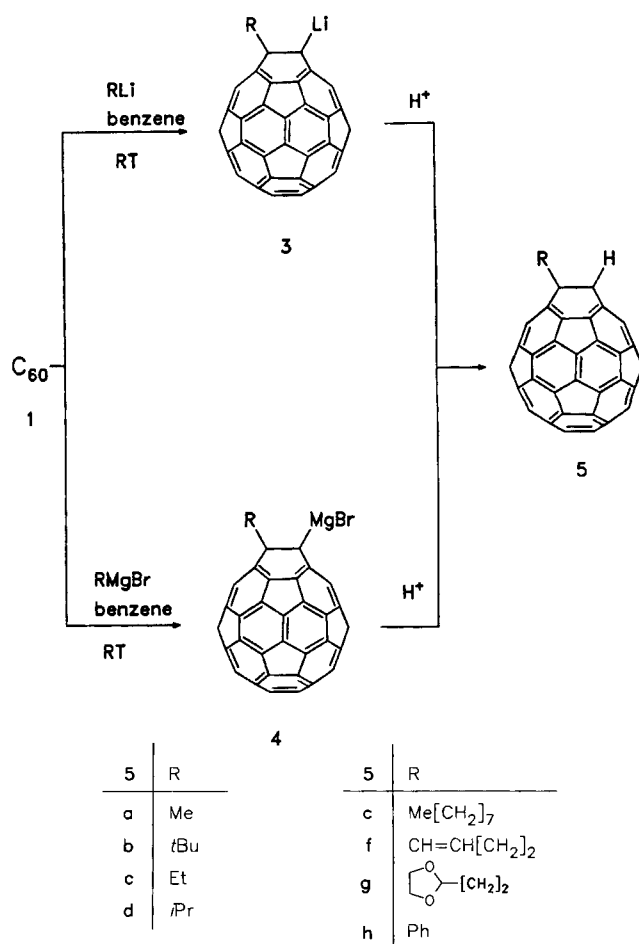
Table 1. Organodihydrofullerenes **5**–**8** synthesized

Compound	Equiv. of nucleophiles used	Yield ^[a] (%)
5a	1.2	47
5b	1.2	51
5c	6.8	80
5d	8.1	56
5e	5.0	67
5f	26.8	63
5g	11.9	52
5h	9.2	74
6	15.1	59
7	1.4	32
8	25.2	60

^[a] Amount of monoaddition products (HPLC) after titration.

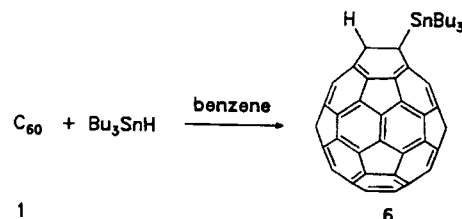
Compounds **5f**, **g** are the first examples of this type of fullerene derivatives carrying functional groups, thus enabling further side-chain chemistry. The protected aldehyde **5g** is useful for a variety of coupling reactions. Because nucleophiles and radicals also react with the monoaddition products of **1** and **2**, the chemical manipulation at the side chains of organodihydrofullerenes will require neutral or acidic conditions. The fullerene core is inert towards dilute proton acids.

The addition of tributyltin hydride to C_{60} (**1**) in benzene requires elevated temperatures (reflux) indicating that a radical mechanism is involved in this hydrostannylation. Tributyltin hydride was added in one step to the benzene so-



RT: room temp.

lution of **1**. Here, the attack to a 6–6 bond in **1** is significantly slower than in the case of the nucleophilic addition. The formation of 1-tributylstannyl-1,9-dihydrofullerene-60 (**6**) was followed by HPLC. After 24 h, the maximum yield (59%) of **6** was reached (Table 1). The latter example shows that also radical additions can be controlled, thus leading to single isomers which can be isolated.



UV/Vis and IR Spectroscopy

The UV/Vis as well as the IR spectra (Figure 1–3) are very characteristic for all monoaddition products synthesized. Particularly in the UV/Vis spectra of **5**, **6** the most intense bands at $\lambda_{max} = 213, 257$ and 326 nm are close to those of C_{60} (**1**), thus demonstrating their electronic similarity (Figure 1). A similar behavior has been observed in other well-defined adducts of C_{60} ^[5,8,9,11]. The biggest changes in the spectra compared to **1** appear in the visible range. The typical features of C_{60} between $\lambda = 400$ and 700 nm are

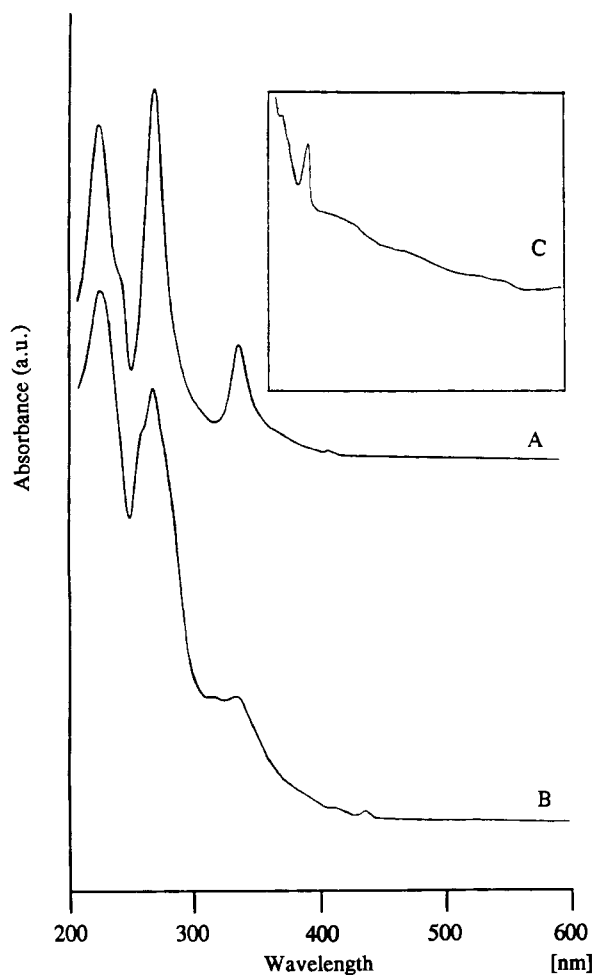


Figure 1. Comparative UV/Vis spectra (hexane) of fullerene-60 (1) (A) and $C_{60}HtBu$ (5b) (B); the inset (C) is the 700–400-nm region of 5b

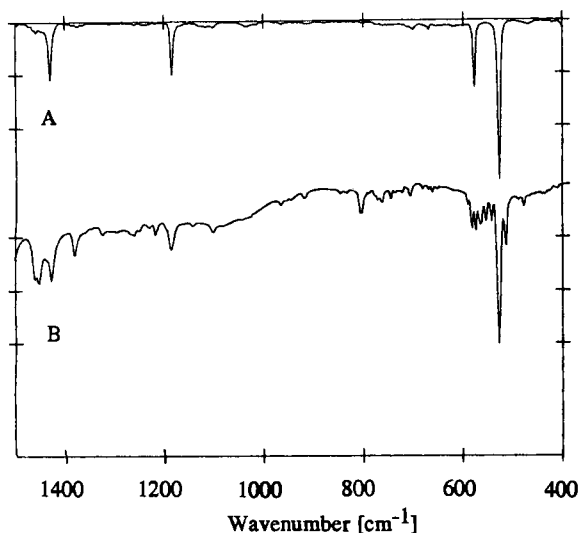


Figure 2. FT-IR spectra (KBr) of fullerene-60 (1) (A) and $C_{60}HEt$ (5c) (B)

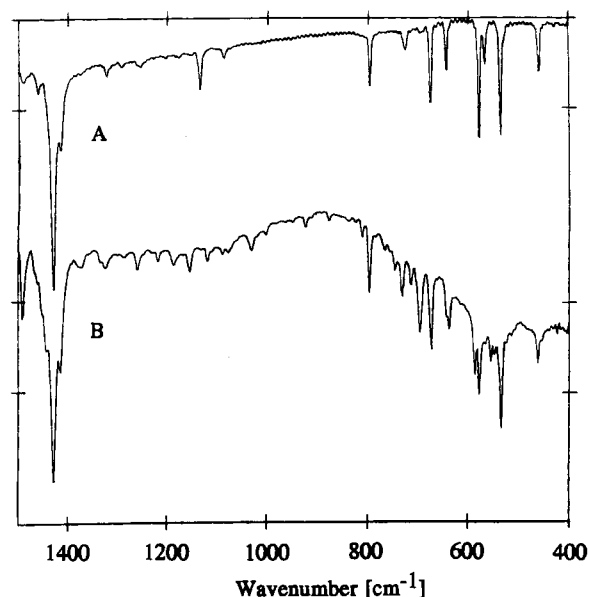


Figure 3. FT-IR spectra (KBr) of fullerene-70 (2) (A) and $C_{70}HPh$ (8) (B)

lost, and a new band at $\lambda_{max} = 435$ nm appears for compounds 5, 6 which is independent of the nature of R. This is the reason for the color change of the solutions from purple (1) to chestnut brown (5–6). The weak band at $\lambda_{max} = 435$ nm was also found in monoadducts of fullerene-60 with C_{2v} symmetry^[10,11]. The UV/Vis spectra of C_{70} (2) are similarly affected upon addition to one double bond. The bands of 6, 7 in the UV spectrum at $\lambda_{max} = 236, 330, 360, 380$ nm become broader. In this case the changes in the visible part are smaller compared to the C_{60} series. Also the color change of the solutions from red to red brown is less pronounced.

Due to the decrease of symmetry from I_h for C_{60} (1) to C_s for 5 and 6 the 4 IR-active T_{1u} modes in 1 at $\tilde{\nu} = 1427, 1183, 576$ and 527 cm^{-1} become broader ($\tilde{\nu} = 1427$ and 1183 cm^{-1}) or split leading to a characteristic pattern between $\tilde{\nu} = 580$ and 514 cm^{-1} (Figure 2). In the case of 7 and 8 the broadening as well as the splitting of the IR band occurs in the whole range of the cluster vibrations between $\tilde{\nu} = 1500$ and 400 cm^{-1} (Figure 3).

¹H-NMR Spectroscopy

In order to achieve a sufficient solubility, the ¹H-NMR spectra of the organodihydrofullerenes 5–8 were recorded in CS_2 solutions with $CDCl_3$ as internal standard. The ¹H-NMR spectra already show that only a single isomer of each fullerene derivative 5–8 has been isolated (Figure 4). One distinct resonance line for the fullereryl proton appears in each spectrum. The remarkable downfield position (between $\delta = 6$ and 7 for 5 and 6 and at $\delta = 4.5$ for 7 and 8) of these peaks demonstrates the electron-withdrawing influence as well as the strain of the fullerene clusters 1 and 2. The chemical shift of the fullereryl proton also depends on the nature of R. Increased sterical requirements, for example on going from $C_{60}HMe$ (5a) to $C_{60}HSnBu_3$ (6), cause a further down-

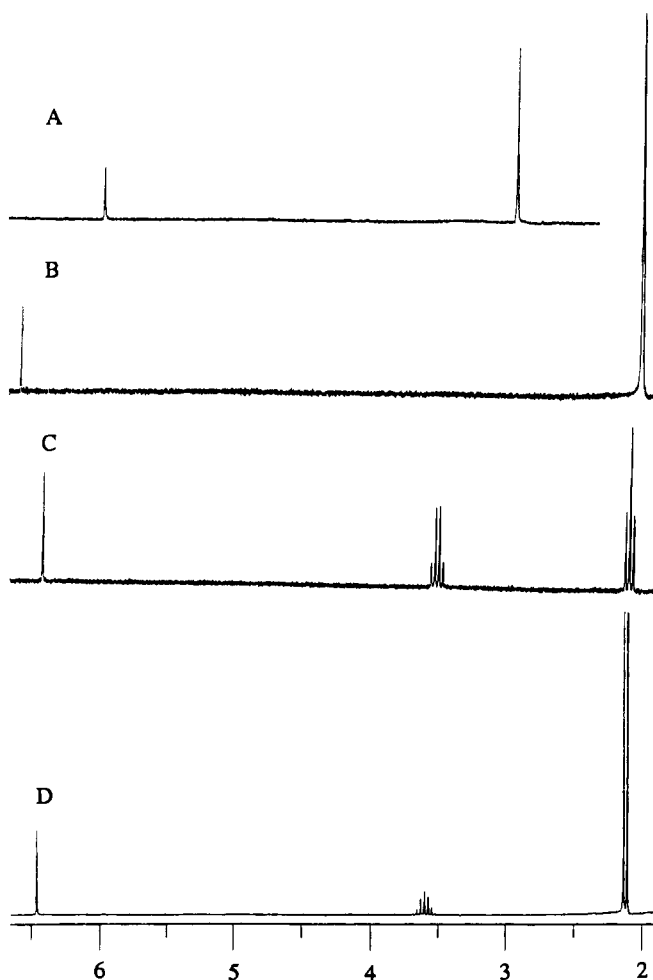


Figure 4. $^1\text{H-NMR}$ spectra (250 MHz, δ scale) of C_{60}HMe (**5a**) (A), C_{60}HtBu (**5b**) (B), C_{60}HtEt (**5c**) (C) and C_{60}HiPr (**5d**) (D) in $\text{CS}_2/\text{CDCl}_3$

Table 2. $^1\text{H-NMR}$ data (δ) of the fullereryl protons in **5a–d**, **6**, **7** with calculated bond angles C-1–C-9–H and energy barriers (ΔE) for the rotation of R

Compound	δ ^[a]	Angle ^[b] [$^\circ$]	ΔE ^[c] [kcal/mol]
5a	6.04	111.07	5.1
5b	6.67	113.31	6.1
5c	6.45	111.91	6.1
5d	6.48	112.44	6.5
6	6.98	113.76	2.4
7	4.42	112.37 ^[d]	5.0 ^[d]
		112.34 ^[e]	4.5 ^[e]

^[a] Chemical shift of the fullereryl proton signal at room temperature. – ^[b] Bond angle between C-1, C-9 and fullereryl-H determined from the MMX-minimized structures. – ^[c] Highest energy barrier for the rotation around the C-9–R bond; determined by stepwise variation (2°) of the dihedral angle C-1–C-9–C–H (**5a**, **c**, **d**, **7**) C-1–C-9–C–C (**5b**) or C-1–C-9–Sn–C (**6**) and MMX minimization of each conformer. – ^[d] For isomer N/3 (R at position N and H at position 3). – ^[e] For isomer 3/N (R at position 3 and H at position N).

field shift of ca. 1 ppm. This remarkable influence of the size of R already indicates that R is located α to H. Molecular modelling (MMX, PCMODEL) shows that the sterical re-

quirement of R also leads to an enhancement of the angle C-1–C-9–H and an increased rotational barrier around the C–R bond (Table 2). Indeed, the $^1\text{H-NMR}$ spectrum of **5b** at -90°C shows a splitting of the resonance lines of the *tert*-butyl groups due to the hindered rotation^[13]. Also the resonance lines of R appear at a comparatively low field (Figure 4). The influence of these effects on the chemical shift of the fullereryl protons in the C_{70} derivatives **7** and **8**, whose signals appear at $\delta = 4.5$, are clearly less important. This indicates that the fullereryl proton is not bound to a carbon atom at the pole (N) being the most “ C_{60} -like” position.

$^{13}\text{C-NMR}$ Spectroscopy

The $^{13}\text{C-NMR}$ spectra were recorded in the presence of $\text{Cr}(\text{acac})_3$ as relaxation reagent. They give unambiguous evidence for the C_s symmetry of C_{60}HR as well as C_{70}HR . The spectrum of C_{60}HiPr (**5d**) (Figure 5) shows distinct signals for C-1 at $\delta = 70.21$ and C-9 at $\delta = 56.95$. The assignment was carried out by performing a J -modulated spin-echo experiment. The number and the intensities of the signals in the region of the quaternary carbon atoms indicate 30 different types of carbon atoms. With the exception of the peaks at $\delta = 147.62$ and 147.45 each resonance line is due to two carbon atoms (C_s symmetry), which are located in the mirror plane. Due to the chemical shift similarity some

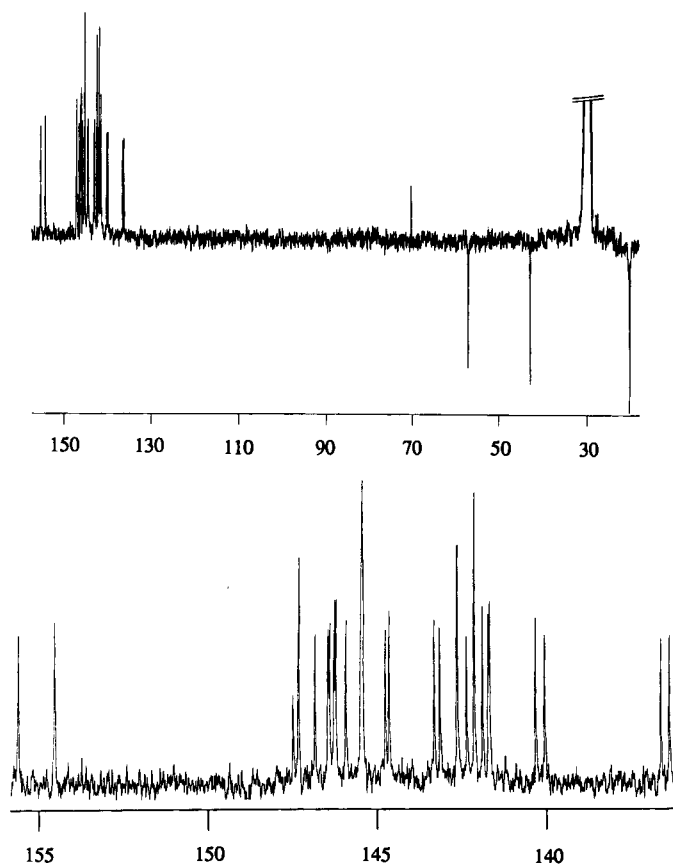


Figure 5. $^{13}\text{C-NMR}$ spectrum (62.9 MHz, δ scale, J -modulated spin-echo experiment) of C_{60}HiPr (**5d**) in $\text{CS}_2/[\text{D}_6]\text{acetone}$ (top); region of the quaternary fullerene carbon atom signals in the $^{13}\text{C-NMR}$ spectrum of **5d** (bottom)

of the peaks are closely overlapping. The signals appearing most downfield-shifted at $\delta = 155.67$ and 154.57 are attributed to the sp^2 carbon atoms C-2, C-5 and C-8, C-10, respectively, being the direct neighbors of the sp^3 centers C-1 and C-9. This assignment has been confirmed by Fagan et al.^[13] who recorded a proton-coupled ^{13}C -NMR spectrum of $C_{60}HtBu$ (**5b**).

The ^{13}C -NMR spectra of the C_{70} derivatives **7** and **8** show an analogous pattern (Figure 6). The signals of the sp^3 carbon atoms in $C_{70}HPh$ (**8**) for example appear at $\delta = 59.83$ [$C(C_{70})-Ph$] and at $\delta = 56.87$ [$C(C_{70})-H$]. 35 peaks are observed in the region of the quaternary C_{70} carbon atoms with two of them (at $\delta = 150.59$ and 148.62) having half intensity. Here also the four direct neighbors of the sp^3 carbon atoms cause two signals which are clearly separated as the most downfield-shifted peaks. These NMR spectra are only consistent with a C_s symmetry of the compounds **7** and **8**. Therefore, either one of the isomers $C_{70}HR$, namely N/3 (1,9) with R bound to the pole (position 1 or N) and H bound to position 9 (carbon of set 3) or 3/N (9,1) with H bound to the pole and R to position 9 was formed. The crystal structure^[16] of the adduct of C_{70} with $[Ir(CO)Cl(PPh_3)_2]$ indeed showed that the addition of the transition metal is an N/3 addition. Calculations on nucleophilic additions to C_{70} ^[15] predicted these isomers N/3 and 3/N among the three most stable for R = H, Me. On the basis of the 1H -NMR data (highfield shift of the fullerenyl-H signal relative to $C_{60}HR$) the formation of the 1,9-isomer is indicated. The final evidence however can only be obtained from single-crystal X-ray data.

In conclusion we have shown that the radialene-cyclohexatriene concept is a useful topological and electronical model to explain the chemical reactivity of fullerene-60. All

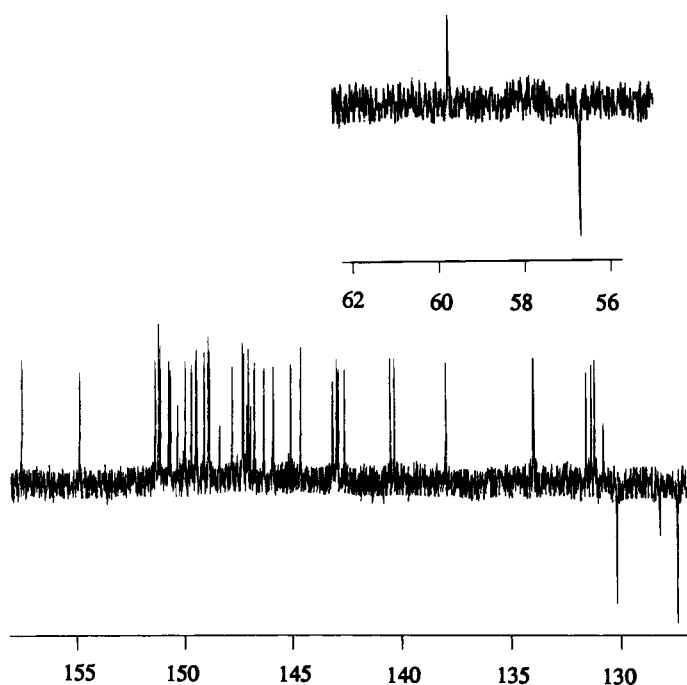
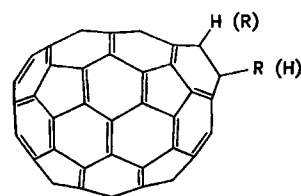


Figure 6. ^{13}C -NMR spectrum (100 MHz, δ scale, J -modulated spin-echo experiment) of $C_{70}HPh$ (**8**) in $CS_2/CDCl_3$



$C_5-C_{70}HR$

7 (R = methyl)

8 (R = phenyl)

the two-step nucleophilic and radical additions presented proceed regioselectively via not delocalized anionic or radical intermediates in 1,9-position. This demonstrates that C_{60} can not be regarded as an aromatic molecule. The addition of nucleophiles and radicals can be used to prepare a large variety of functionalized 1,9-dihydrofullerene-60 derivatives. Also the nucleophilic additions to C_{70} are regioselective and take place at the most " C_{60} -like" double bond between the pole N and a carbon atom of set 3, thus forming the derivatives $C_5-C_{70}HR$ as isomerically pure single compounds.

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Experimental

Fullerene-rich soot was prepared according to the graphite-arc vaporisation method^[17] by employing a simple bench-top reactor^[18]. Pure C_{60} (>99%) and C_{70} (>98%) were obtained by soxhlet chromatography^[19] and subsequent washing with hexane. — All fullerene addition reactions were run under N_2 . The commercially available $tBuLi$ (1.7 M in pentane) and $MeLi$ (1.6 M in Et_2O) were used as obtained. Benzene was purified by refluxing over CaH_2 and distillation. The Grignard solutions (1 M in THF) were freshly prepared under N_2 from the corresponding commercially available bromides. — HPLC was performed with the Beckman System Gold: Autosampler 507, Programable Solvent Module 126, Diode-Array Detector Module 168. Experimental conditions for the reaction control: Beckman reversed-phase column C18, ultrasphere ODS with the dimensions 25×0.46 cm, particle size $5 \mu m$, eluent $CHCl_3/MeCN$ (60:40), pressure 8000 kPa, flow rate 1 ml min^{-1} , detection at $\lambda = 340$ nm and with several diode-array scans. — UV/Vis: Shimadzu UV-65. FT-IR: Bruker IFS 48. 1H NMR: Bruker AC 250 (250 MHz), Bruker WM 400 (400 MHz); internal standard: $CDCl_3$. ^{13}C NMR: Bruker AC 250 (62.9 MHz), Bruker WM 400 (100 MHz); $Cr(acac)_3$ dissolved in $CS_2/CDCl_3$ (80:20) or $CS_2/[D_6]acetone$ (80:20) was used as a relaxation reagent; internal standard: CS_2 ($\delta = 192.80$). MS: Varian MAT 711; the method of ionization was either field desorption (FD) or fast-atom bombardment (FAB). Elemental analyses: Carlo Erba Analyser 1104 and 1106.

General Procedure for the Preparation of 1-Alkyl-1,2-dihydrofullerenes-60 5a–g, 1-Phenyl-1,9-dihydrofullerene-60 (5b), C_5 -Methyldihydrofullerene-70 (7) and C_5 -Phenyldihydrofullerene-70 (8): In a dry 250-ml two-necked flask equipped with an N_2 inlet C_{60} (**1**) (30 mg, 0.042 mmol) or C_{70} (**2**) (35 mg, 0.042 mmol) was dissolved in benzene (50 ml). From this solution 200 μl was used to prepare a dilution series in hexane (1.66, 0.83, 0.42, and 0.17 [10^{-5} mol l^{-1}] in 10 ml) for HPLC calibration. The nucleophiles $tBuLi$ and $MeLi$ were added in portions of 0.2 equiv. relative to **1** and **2**. The Grig-

nard compounds in THF were added in larger portions (0.3–2.0 equiv.). Rapid stirring is important to minimize side reactions by high local concentrations of the nucleophiles in the reaction mixture. After each addition step of the nucleophiles, 200 μ l of the reaction mixture was removed, quenched with 0.01 M HCl (200 μ l) in MeOH, and diluted with hexane to 10 ml for HPLC analysis. The extinction coefficients ($\epsilon = 23000$ for C_{60} HR, 28500 for C_{70} HR) at the detection wavelength are essentially the same for all compounds synthesized. After the titration, the reaction mixture was quenched with 0.01 M HCl (4 ml) in MeOH causing the dark precipitate of the fullerides **3**, **4** and $C_{70}R^-$ to dissolve. After evaporation of the solvent, the compounds were purified by flash chromatography with hexane/toluene (95:5) (**5d,h**) hexane/toluene (90:10) (**5a**), hexane/toluene (80:20) (**7,8**) and hexane/ $CHCl_3$ (30:70) (**5g**). The compounds **5b**, **c**, **e**, and **f** were purified by preparative HPLC. Experimental conditions: Beckman reversed-phase column C18, ultrasphere with the dimensions 25 \times 1 cm, particle size 5 μ m, eluent $CHCl_3/CH_3CN$ (60:40) pressure 7600 kPa, flow rate 3.2 ml min^{-1} , detection at $\lambda = 340$ nm.

1-Methyl-1,9-dihydrofullerene-60 (5a): UV/Vis (hexane): $\lambda_{max} = 213$ nm, 258, 329, 406 (sh), 435. — IR (KBr): $\tilde{\nu} = 2953$ cm^{-1} , 2924, 2845, 1514, 1462, 1427, 1377, 1182, 581, 561, 553, 542, 527, 513. — 1H NMR ($CS_2/CDCl_3$): $\delta = 6.04$ (s, 1H, fullereryl-H), 2.97 (s, 3H, CH_3). — ^{13}C NMR ($CS_2/CDCl_3$): $\delta = 157.83, 154.49, 147.88, 147.74, 147.69, 147.16, 146.78, 146.46, 146.34, 146.27, 145.66, 145.64, 144.26, 144.02, 143.53, 143.11, 142.97, 142.64, 140.55, 140.27, 136.54, 135.41, 70.08$ [s, 1C, $C(C_{60})-CH_3$], 62.04 [s, 1C, $C(C_{60})-H$], 30.24, (s, 1C, CH_3). — MS (FD), m/z (%): 736 (100) [M^+], 720 (43) [$M^+ - H - CH_3$].

$C_{61}H_4$ (736.7) Calcd. C 99.45 H 0.55
Found C 98.45 H 0.41

1-tert-Butyl-1,9-dihydrofullerene-60 (5b)⁹¹: UV/Vis (hexane): $\lambda_{max} = 213$ nm, 248 (sh), 257, 308 (sh), 226, 408 (sh), 425, 464, 484, 640. — IR (KBr): $\tilde{\nu} = 2959$ cm^{-1} , 2922, 2866, 1462, 1427, 1396, 1369, 1188, 1094, 902, 763, 730, 582, 567, 553, 542, 526, 513. — 1H NMR ($CS_2/CDCl_3$): $\delta = 6.67$ (s, 1H, fullereryl-H), 2.09 (s, 9H, CH_3). — MS (FAB), m/z (%): 779 (15) [M^+], 720 (100) [$M^+ - H - tBu$].

$C_{64}H_{10}$ (778.8) Calcd. C 98.71 H 1.29
Found C 98.82 H 0.97

1-Ethyl-1,9-dihydrofullerene-60 (5c)⁹¹: UV/Vis (hexane): $\lambda_{max} = 214$ nm, 248 (sh), 258, 308 (sh), 326, 408 (sh), 436, 465, 484, 640. — IR (KBr): $\tilde{\nu} = 2959$ cm^{-1} , 2922, 2866, 1452, 1427, 1380, 1261, 1184, 1101, 580, 572, 563, 553, 542, 526, 514. — 1H NMR ($CS_2/CDCl_3$): $\delta = 6.45$ (s, 1H, fullereryl-H), 3.52 (q, $J = 7$ Hz, 2H, CH_2CH_3), 2.09 (t, $J = 7$ Hz, 3H, CH_2CH_3). — MS (FAB) m/z (%): 750 (20) [M^+], 748 (25) [$M^+ - 2H$], 721 (100) [$M^+ - C_2H_5$].

1-Isopropyl-1,9-dihydrofullerene-60 (5d): UV/Vis (hexane): $\lambda_{max} = 244$ (sh), nm, 254, 307 (sh), 433. — IR (KBr): $\tilde{\nu} = 2959$ cm^{-1} , 2922, 2849, 1462, 1429, 1386, 1371, 1261, 1217, 1188, 1122, 767, 590, 574, 563, 553, 541, 528, 517. — 1H NMR ($CS_2/CDCl_3$): $\delta = 6.48$ (s, 1H, fullereryl-H), 3.60 [sept, $J = 7$ Hz, 1H, $CH(CH_3)_2$], 2.12 (d, $J = 7$ Hz, 6H, $CH(CH_3)_2$). — ^{13}C NMR ($CS_2/[D_6]acetone$): $\delta = 155.67$ (s, 2C, C_{60}), 154.57 (s, 2C, C_{60}), 147.62 (s, 1C, C_{60}), 147.45, 147.46 (two closely overlapping signals, 3C, C_{60}), 146.95 (s, 2C, C_{60}), 146.60, 146.55 (2 s, 4C, C_{60}), 146.42, 146.46 (2 s, 4C, C_{60}), 146.05 (s, 2C, C_{60}), 145.61 (three closely overlapping signals, 6C, C_{60}), 144.90 (s, 2C, C_{60}), 144.79 (s, 2C, C_{60}), 143.46 (s, 2C, C_{60}), 143.29 (s, 2C, C_{60}), 142.79 (s, 4C, C_{60}), 142.50 (s, 2C, C_{60}), 142.28 (s, 4C, C_{60}), 142.02 (s, 2C, C_{60}), 141.86 (s, 2C, C_{60}), 141.82 (s, 2C, C_{60}), 140.48 (s, 2C, C_{60}), 140.20 (s, 2C, C_{60}), 136.78 (s, 2C, C_{60}), 136.51 (s, 2C, C_{60}), 70.21 [s,

1C, $C(C_{60})-CH(CH_3)_2$], 56.95 [s, 1C, $C(C_{60})-H$], 42.80 [s, 1C, $CH(CH_3)_2$], 19.93 [s, 2C, $CH(CH_3)_2$]. — MS (FD) m/z (%): 765 (100) [M^+], 720 (15) [$M^+ - H - C_3H_7$].

$C_{63}H_8$ (764.8) Calcd. C 98.95 H 1.05
Found C 98.79 H 0.82

1-Octyl-1,9-dihydrofullerene-60 (5e): UV/Vis (hexane): $\lambda_{max} = 215$ nm, 249 (sh), 258, 328, 435. — IR (KBr): $\tilde{\nu} = 2922$ cm^{-1} , 2851, 1462, 1437, 1375, 1261, 1182, 1094, 1026, 804, 582, 574, 561, 542, 527, 514. — 1H NMR ($CS_2/CDCl_3$): $\delta = 6.41$ (s, 1H, fullereryl-H), 3.38 (m, 2H, CH_2), 2.52 (m, 2H, CH_2), 1.81 (m, 2H, CH_2), 1.61 (m, 2H, CH_2), 1.50–0.70 (m, 9H, CH_2 , CH_3). — MS (FD) m/z (%): 835 (100) [M^+], 720 (14) [$M^+ - H - C_8H_{17}$].

1-(3-Butenyl)-1,9-dihydrofullerene-60 (5f): UV/Vis (hexane): $\lambda_{max} = 211$ nm, 253, 326, 432, 600. — IR (KBr): $\tilde{\nu} = 3080$ cm^{-1} , 2923, 2867, 1460, 1427, 1215, 1182, 912, 775, 730, 582, 572, 563, 553, 544, 527, 514. — 1H NMR ($CS_2/CDCl_3$): $\delta = 6.49$ (s, 1H, fullereryl-H), 6.33 (m, 1H, CH), 5.49 [d, $J = 17$ Hz, 1H, (E)-CH], 5.31 [d, $J = 10$ Hz, 1H, (Z)-CH], 3.53 (m, 2H, CH_2), 3.36 (m, 2H, CH_2). — MS (FAB) m/z (%): 777 (25) [M^+], 720 (100) [$M^+ - H - C_4H_7$].

$C_{64}H_8$ (776.8) Calcd. C 98.96 H 1.04
Found C 96.24 H 0.37

1-[2-(1,3-Dioxolan-2-yl)ethyl]-1,9-dihydrofullerene-60 (5g): UV/Vis (hexane): $\lambda_{max} = 214$ nm, 257, 330, 435. — IR (KBr): $\tilde{\nu} = 2923$ cm^{-1} , 2866, 1462, 1427, 1315, 1215, 1182, 1140, 1031, 759, 719, 580, 572, 563, 553, 527, 514. — 1H NMR ($CS_2/CDCl_3$): $\delta = 6.41$ (s, 1H, fullereryl-H), 5.32 (t, $J = 4$ Hz, 1H, CH), 4.12 (m, 2H, CH_2), 4.00 (m, 2H, CH_2), 3.51 (m, 2H, CH_2), 2.88 (m, 2H, CH_2). — MS (FD) m/z (%): 823 (100) [M^+], 720 (24) [$M^+ - H - C_5H_9O_2$].

$C_{65}H_{10}O_2$ (822.8) Calcd. C 94.89 H 1.23
Found C 94.51 H 1.53

1-Phenyl-1,9-dihydrofullerene-60 (5h): UV/Vis (hexane): $\lambda_{max} = 222$ nm, 252, 327, 432, 611. — IR (KBr): $\tilde{\nu} = 3055$ cm^{-1} , 3022, 1490, 1458, 1427, 1226, 1182, 846, 742, 727, 694, 590, 576, 564, 551, 527, 514. — 1H NMR ($CS_2/CDCl_3$): $\delta = 8.50$ (dd, $J = 8$ Hz and $J = 1$ Hz, 2H, phenyl-H), 7.80 (m, 2H, phenyl-H), 7.64 (m, 1H, phenyl-H), 6.81 (s, 1H, fullereryl-H). — MS (FD) m/z (%): 789 (100) [M^+], 720 (40) [$M^+ - H - C_6H_5$].

Synthesis of 1-Tributylstannyl-1,9-dihydrofullerene-60 (6): In a dry 250-ml two-necked flask equipped with an N_2 inlet and a reflux condenser **1** (30 mg, 0.042 mmol) was dissolved in benzene (50 ml) under N_2 . To this solution Bu_3SnH (200 μ l, 0.635 mmol) was added. The mixture was refluxed with stirring for 24 h. The formation of **6** and the consumption of **1** was followed by HPLC (peak detection at $\lambda = 340$ nm). After evaporation of the solvent, **6** was purified by preparative HPLC (conditions vide supra). — UV/Vis (hexane): $\lambda_{max} = 222$ nm, 252, 328, 432. — IR (KBr): $\tilde{\nu} = 2950$ cm^{-1} , 2852, 1502, 1461, 1427, 1375, 1232, 1182, 1043, 698, 671, 574, 561, 553, 543, 527, 513. — 1H NMR ($CS_2/CDCl_3$): $\delta = 6.98$ (s, 1H, fullereryl-H), 1.6–0.8 (m, 27H, butyl-H). — MS (FD) m/z (%): 720 (100) [$M^+ - H - SnBu_3$].

$C_{72}H_{28}Sn$ (1011.5) Calcd. C 85.48 H 2.79
Found C 84.96 H 3.36

***C*-Methyldihydrofullerene-70 (7)**: UV/Vis (hexane): $\lambda_{max} = 330$ nm (sh), 378, 392, 450, 540 (sh). — IR (KBr): $\tilde{\nu} = 2960, 2922, 2866, 1429, 1275, 1323, 1259, 1220, 1117, 1085, 814, 795, 765, 729, 669, 640, 576, 547, 534, 476, 459$. — 1H NMR ($CS_2/CDCl_3$): $\delta = 4.42$ (s, 1H, fullereryl-H), 2.59 (s, 3H, CH_3). — ^{13}C NMR ($CS_2/CDCl_3$): $\delta = 158.43$ (s, 2C, C_{70}), 155.30 (s, 2C, C_{70}), 151.95 (s, 2C, C_{70}), 151.44 (s, 2C, C_{70}), 151.28 (s, 2C, C_{70}), 150.96 (s, 2C, C_{70}), 150.84 (s, 2C, C_{70}), 150.56 (s, 1C, C_{70}), 150.05 (s, 2C, C_{70}), 149.87 (s, 2C, C_{70}), 149.67 (s,

2C, C₇₀), 149.49 (s, 2C, C₇₀), 149.09 (s, 2C, C₇₀), 149.04 (s, 2C, C₇₀), 148.01 (s, 1C, C₇₀), 147.69 (s, 2C, C₇₀), 147.46 (s, 2C, C₇₀), 147.28 (s, 2C, C₇₀), 146.89 (s, 2C, C₇₀), 146.70 (s, 2C, C₇₀), 146.50 (s, 2C, C₇₀), 146.00 (s, 2C, C₇₀), 145.29 (s, 2C, C₇₀), 144.50 (s, 2C, C₇₀), 143.28 (s, 2C, C₇₀), 143.04, 143.02 (two closely overlapping signals, 4C, C₇₀), 142.62 (s, 2C, C₇₀), 140.44 (s, 2C, C₇₀), 140.17 (s, 2C, C₇₀), 138.22 (s, 2C, C₇₀), 134.04 (s, 2C, C₇₀), 131.54 (s, 2C, C₇₀), 131.27, 131.25 (two closely overlapping signals, 4C, C₇₀), 55.94 [s, 1C, C(C₇₀)-CH₃], 51.47 [s, 1C, C(C₇₀)-H], 30.70 (s, 1C, CH₃). — MS (FD) *m/z* (%): 857 (30) [M⁺], 840 (100) [M⁺ - H - CH₃].

C₇₁H₄ (856.8) Calcd. C 99.53 H 0.47

Found C 96.93 H 0.38

*C*₅-Phenyldihydrofullerene-70 (8): UV/Vis (hexane): λ_{max} = 236 nm, 330, 360 (sh), 380, 396 (sh), 460, 545 (sh). — IR (KBr): ν̄ = 3053 cm⁻¹, 3022, 1490, 1429, 1323, 1259, 1217, 1153, 1118, 1087, 1029, 921, 875, 808, 795, 744, 729, 711, 694, 671, 636, 584, 577, 554, 532, 461. — ¹H NMR (CS₂/CDCl₃): δ = 8.08 (d, *J* = 8 Hz, phenyl-H), 7.66 (m, 2H, phenyl-H), 7.53 (m, 1H, phenyl-H), 4.69 (s, 1H, fullerene-H). — ¹³C NMR (CS₂/CDCl₃): δ = 157.89 (s, 2C, C₇₀), 155.20 (s, 2C, C₇₀), 151.65 (s, 2C, C₇₀), 151.48 (s, 2C, C₇₀), 151.41 (s, 2C, C₇₀), 151.00 (s, 2C, C₇₀), 150.91 (s, 2C, C₇₀), 150.59 (s, 1C, C₇₀), 150.22 (s, 2C, C₇₀), 149.92 (s, 2C, C₇₀), 149.72 (s, 2C, C₇₀), 149.34 (s, 2C, C₇₀), 149.15 (s, 2C, C₇₀), 149.10 (s, 2C, C₇₀), 148.62 (s, 1C, C₇₀), 148.05 (s, 2C, C₇₀), 147.58 (s, 2C, C₇₀), 147.52 (s, 2C, C₇₀), 147.30 (s, 2C, C₇₀), 147.02 (s, 2C, C₇₀), 146.58 (s, 2C, C₇₀), 146.15 (s, 2C, C₇₀), 145.35 (s, 2C, C₇₀), 144.90 (s, 2C, C₇₀), 143.42 (s, 2C, C₇₀), 143.25 (s, 2C, C₇₀), 143.16 (s, 2C, C₇₀), 142.88 (s, 2C, C₇₀), 140.76 (s, 2C, C₇₀), 140.55 (s, 2C, C₇₀), 138.18 (s, 2C, C₇₀), 134.13 (s, 2C, C₇₀), 131.67 (s, 2C, C₇₀), 131.42 (s, 2C, C₇₀), 131.27 (s, 2C, C₇₀), 130.87 (s, 1C, phenyl-C), 130.24 (s, 2C, phenyl-C), 128.26 (s, 1C, phenyl-C), 127.46 (s, 2C, phenyl-C), 59.83 [s, 1C, C(C₇₀)-phenyl], 56.87 [s, 1C, C(C₇₀)-H]. — MS (FD) *m/z* (%): 919 (100) [M⁺], 80 (25) [M⁺ - H - C₆H₅].

C₇₆H₆ (918.9) Calcd. C 99.34 H 0.66

Found C 96.97 H 0.52

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