# Cycloaddition of diazocycloalkanes to [60]fullerene in the presence of Pd-containing complex catalyst

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A catalytic method for the selective and efficient synthesis of cycloalkylidenehomofullerenes by cycloaddition of [60]fullerene to diazocycloalkanes generated *in situ* from the corresponding hydrazones in the presence of a complex catalytic system [$Pd(acac)_2$—$PPh_3$—$Et_3Al$] has been developed.

**Key words:** metal complex catalysis, cycloaddition, [60]fullerene, diazo compounds, cycloalkylidenehomofullerene, spirohomofullerene.

Despite the fact that homofullerenes are formed under kinetic control and methanofullerenes are more thermally stable products of the reaction of [60]fullerene with diazo compounds, the isolation of 5,6-open adducts in the individual state is practically impossible. The only exceptions are the synthesis of homofullerenes by cycloaddition of diazomethane and other diazo compounds, which were generated *in situ* from the salts of the corresponding tosylhydrazones, to [60]fullerene.[1—6] The significant disadvantages of the known synthetic methods towards homofullerenes are low selectivity,[3—6] high sensitivity to changes in the temperature and the reaction time and low yields of the target cycloadducts.

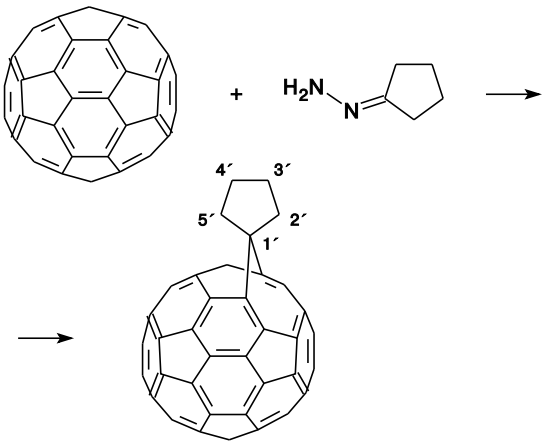
Recently,[7—9] we have reported the selective synthesis of homo- and methanofullerenes in high yields by cycloaddition of diazomethane,[7] diazoalkanes,[8] and diazoacetates[9] to [60]fullerene in the presence of the palladium complexes. This reaction carried out in the presence of $Pd(acac)_2$—$PPh_3$—$AlEt_3$ (1 : 4 : 4) at 80 °C furnished exclusively thermodynamically more stable 6,6-closed cycloadducts (methanofullerenes). In continuation of this research, and with aim at studying the possibility of the synthesis of spirohomo- and spiromethanofullerenes, in the present work we investigated cycloaddition of diazocycloalkanes, which were generated *in situ* by oxidation of the corresponding ketone hydrazones employing the known procedure,[10—12] to [60]fullerene in the presence of the complex catalyst $Pd(acac)_2$—$PPh_3$—$Et_3Al$. The effect of the size of the cycle in starting diazo compound on the yield and selectivity of mono- and dicycloaddition has also been studied.

## Results and Discussion

A three-component catalyst prepared from $Pd(acac)_2$, $PPh_3$ and $Et_3Al$ in a 1 : 2 : 4 ratio, respectively, turned out to be particularly efficient in the reactions of [60]fullerene with diazocycloalkanes and substituted diazomethanes. In this regard, all subsequent experiments were carried out using this catalytic system.

It has been found* that the reaction of [60]fullerene with diazocyclopentane, which was generated *in situ* by oxidation of cyclopentanone hydrazone with $MnO_2$ (1 : 1.5 molar ratio), in the presence of a three-component catalyst $Pd(acac)_2$—$PPh_3$—$Et_3Al$ (1 : 2 : 4, 20 mol.%) at ~20 °C (1.5 h, toluene) resulted exclusively in spirohomofullerene **1** in ~70% yield (Scheme 1). Probably, the

**Scheme 1**




**1**

**Reagents and conditions:** $Pd(acac)_2$ : $PPh_3$ : $Et_3Al$ = 1 : 2 : 4, $MnO_2$, 20 °C, 1.5 h.

* Here and elsewhere the yields are given on the amount of the starting [60]fullerene used in the reactions.

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formation of homofullerene is due to the lower content of the phosphinic ligand and lower reaction temperature. A more detailed explanation of this issue requires further study. Increase in the reaction time to 2 h resulted in the cycloadducts formed due to diaddition. No presence of the cycloadduct of [60]fullerene and diazopentane formed at the 6,6-bond of the staring carbon cluster was detected even at elevation of the reaction temperature to 80 °C. The reaction under study carried out under the same conditions but without catalyst afforded cycloadduct **1** in a yield less than 30%.

The structure of compound **1** was confirmed based on the data from MALDI—TOF negative-ion mass spectrometry, 1D and 2D NMR experiments ($^1$H, $^{13}$C, COSY, HSQC, and HMBC), and UV spectroscopy as well.

Thus, the $^1$H NMR spectrum of spirohomofullerene **1** revealed the symmetrical eight spin system of the bounded hydrogen atoms, which was by means of the COSY spectrum attributed to the spirocyclopentane fragment located in the plane of symmetry of the molecule. In contrast to the proton of the methylene group, ($\delta_H$ $CH_2(5')$ = 3.99), which located above the plane of the five-membered ring of [60]fullerene, the *syn*-oriented protons of the methylene group located above the plane of the six-membered ring of the fullerene core are significantly shielded ($\delta_H$ $CH_2(2')$ = 1.69). Relative to the methylene group ($\delta_C$ $CH_2(5')$ = 43.08), the diastereotopic carbon atom of the methylene group with *syn*-orientation to six-membered fragment has the similar shielding ($\delta_C$ $CH_2(2')$ = 35.88). For β-carbon atoms, the diastereotopic splitting decreases to 0.1 ppm, while in the proton spectra the difference in the shielding is $\Delta_{dias} = \delta_H(CH_2(4')) - \delta_H(CH_2(3')) = 0.3$ ppm. The structure of **1** has one plane of symmetry, which led to a decrease in the number of the signals in the $^{13}$C NMR to 24. In the HMBC spectra (Fig. 1), correlation peaks of α-protons of the spiropentane fragment with the spiro C(1′) atom ($\delta_C$ = 57.49) and the bridgehead C(1) and C(2) atoms ($\delta_C$ = 143.87) of the fullerene core were observed.

The absence of the signal in the range of δ 80—85 in the $^{13}$C NMR and the weak absorption band at 420—430 nm in the UV spectra clearly indicated formation of the open cycloadduct at 5,6-bond of [60]fullerene. Mass spectra of the resulting adduct of [60]fullerene revealed the molecular ion with 788.724 $[M]^-$ (calculated 788.759) and fragment ion with *m/z* 720.642 $[C_{60}]^-$, which confirmed the formation of the suggested mono adduct.

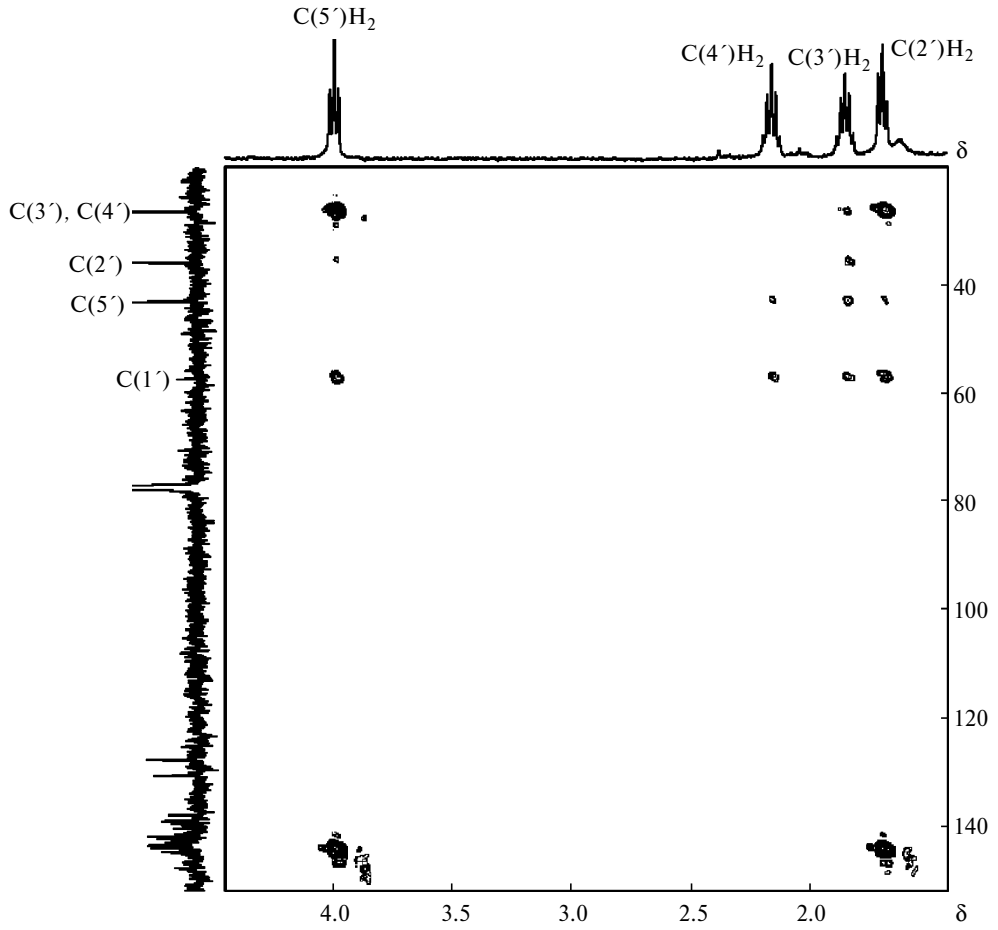



**Fig. 1.** HMBC-experiment of spirohomofullerene **1** (400.13 MHz for $^1$H, 100.62 MHz for $^{13}$C, solvent — $CS_2$ : $CDCl_3$ = 5 : 1).

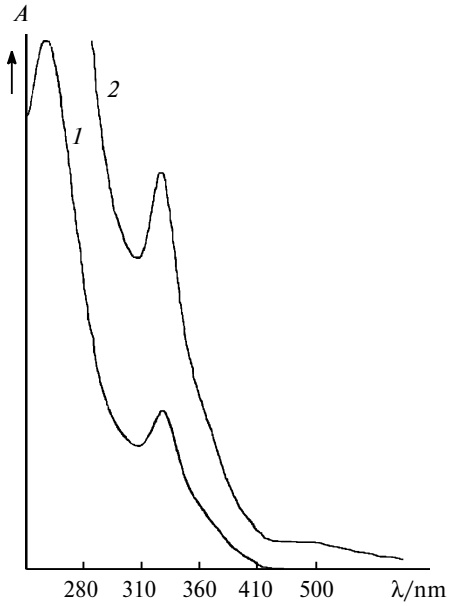
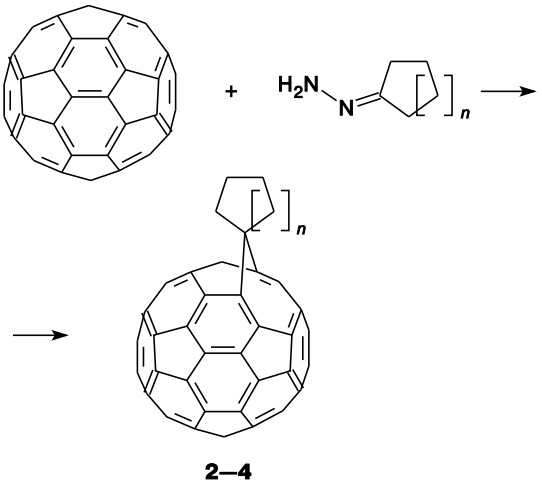



**Fig. 2.** UV spectra of spirohomofullerene **1**. Concentrations of **1** in $CDCl_3$ are $3 \cdot 10^{-4}$ (*1*) and $9 \cdot 10^{-4}$ mol $L^{-1}$ (*2*).

The reactions of [60]fullerene with diazo compounds derived from hydrazones of cyclohexanone, cycloheptanone and cyclooctanone were performed according to the above described procedure. It was found, that under developed conditions (~20 °C, 1.5 h, toluene, 20 mol.% of $Pd(acac)_2$—$2PPh_3$—$4Et_3Al$) diazocyclohexane, diazocycloheptane and diazocyclooctane, which were generated *in situ* from the mentioned above cyclic ketones, react with [60]fullerene to give cycloalkylidenehomofullerene **2—4** in 70—80% yields (Scheme 2). No significant effect of the cycle size on the selectivity and the direction of the reaction were found. It was shown, that diazocyclododecanone does not react with [60]fullerene under described conditions, which can probably be explained by sterical hindrance.

The resulting spirohomofullerenes **1—4** underwent thermal isomerization by refluxing in toluene for 12 h to give the corresponding individual spiromethanofullerenes **5—8** in quantitative yields (Scheme 3).

**Scheme 2**

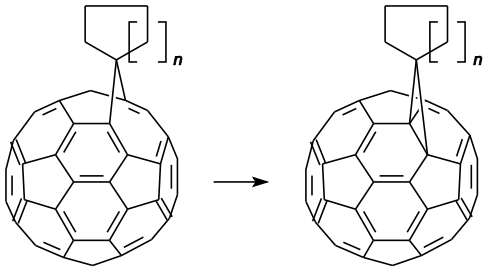



**2—4**

*n* = 2 (**2**), 3 (**3**), 4 (**4**)

**Reagent and conditions:** $Pd(acac)_2 : PPh_3 : Et_3Al = 1 : 2 : 4$, $MnO_2$, 20 °C, 1.5 h.

**Scheme 3**




**1—4** **5—8**

*n* = 1 (**1**, **5**), 2 (**2**, **6**), 3 (**3**, **7**), 4 (**4**, **8**)

**Reagent and conditions:** 110 °C, 12 h, toluene.

In the UV spectra of individual compounds **5—8**, the narrow absorption band of low intensity at 430 nm was observed, which is fairly simple and reliable evidence of 6,6-closed adduct formation (Fig. 3).

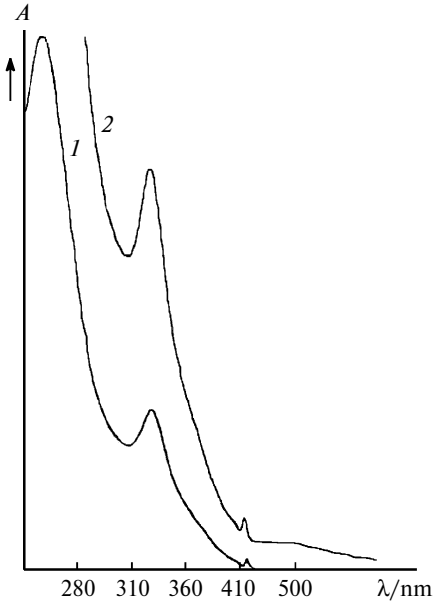



**Fig. 3.** UV spectra of spiromethanofullerenes **5—8**. Concentrations of **5—8** in $CDCl_3$ are $3 \cdot 10^{-4}$ (*1*) and $9 \cdot 10^{-4}$ mol $L^{-1}$ (*2*).

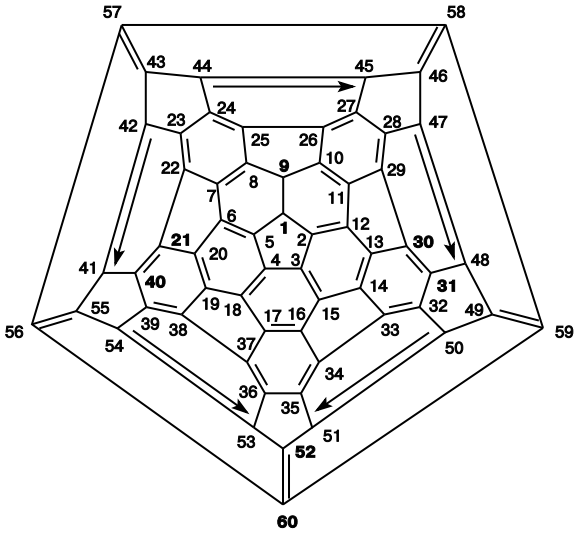



**Fig. 4.** The Schlegel diagram for methanofullerene **5** with the pairwise equivalent carbon atoms.

As it shown on the Schlegel diagram for 6,6-closed isomer **5**, existence of two planes of symmetry passed through the cyclopropane and spirocyclopentane fragments of the molecule led to the pairwise equivalence of eight carbon atoms (C(1)—C(9) and C(52)—C(60), C(21) and C(30), C(40) and C(31)) of the fullerene core, which located in the planes of element symmetry (Fig. 4), and thirteen nonequivalent groups containing four carbon atoms each.

The $^{13}C$ NMR spectra of cycloadduct **5** contained 17 nonequivalent signals for the fullerene core, four of which have double intensity and 13 signals have quadruple intensity. This pattern of the spectra is in full agreement with elements of symmetry of methanofullerene **5**. The signal for the quaternary $sp^3$-hybridized carbon atoms of the fullerene core $\delta_C = 82.61$ of double intensity has a pronounced cross-peak in HMBC spectra resulted from vicinal coupling with the hydrogen atoms $\delta_H$(C(2′) and C(5′)) = 2.91. The latter signal in HMBC spectra has also the cross-peaks with the spiro carbon atom $\delta_C$ C(1′) = 49.05 resulted from geminal spin-spin coupling.

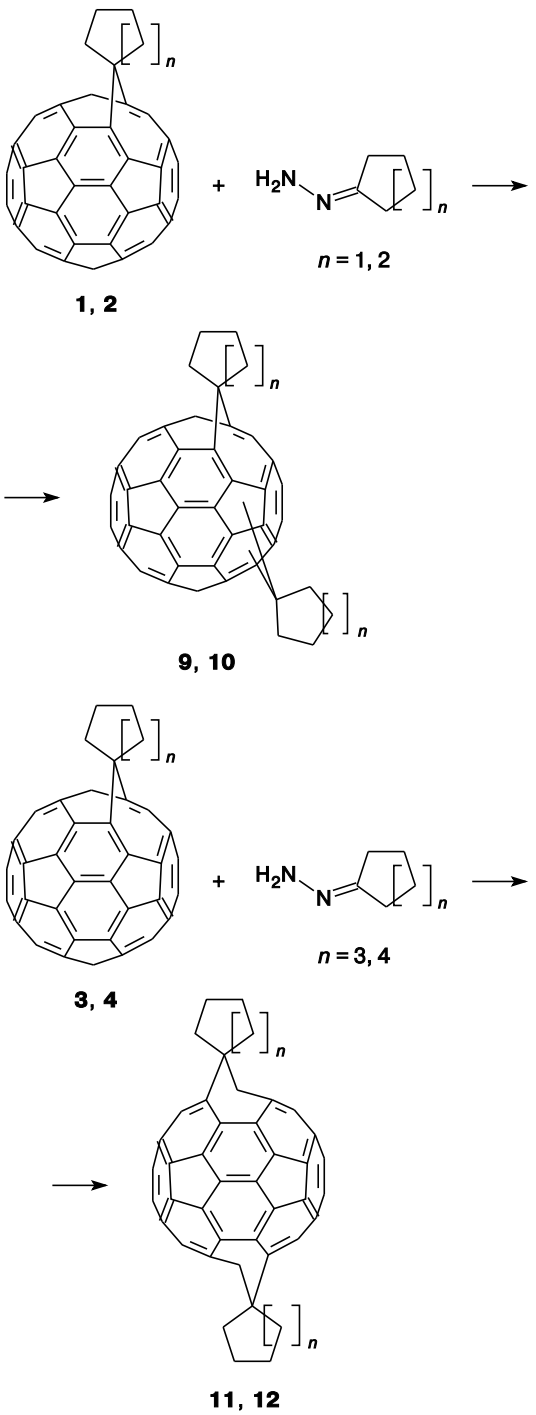
Similar results were obtained for cyclohexylidene (**2**, **6**), cycloheptylidene (**3**, **7**), and cyclooctylidene (**4**, **8**) fullerene derivatives.

Mass spectra of compound **5** revealed the molecular ion peak with *m/z* 788.719 $[M]^-$ (calculated 788.759) and the fragment ion of the fullerene core with *m/z* 720.642 formed by the cleavage of the attached addend.

It was predicted by means of calculations[13] that bis-spiromethanofullerene with the addends located in the *trans*-1 position is promising as an inhibitor of HIV-1 protease.

With the aim at synthesizing the symmetrical bis-spiroadducts, we studied the cycloaddition of the second molecule of diazocycloalkanes to the corresponding

**Scheme 4**




*n* = 1 (**9**), 2 (**10**), 3 (**11**), 4 (**12**)

**Reagent and conditions:** $Pd(acac)_2 : PPh_3 : Et_3Al = 1 : 2 : 4$, $MnO_2$, 20 °C, 1.5 h.

mono-adducts **1—4**. It was found that the reactions of diazocyclopentane or diazocyclohexane, which were generated *in situ* by oxidation of the corresponding

hydrazones, with spirohomofullerenes **1** or **2** resulted in a mixture of regioisomeric bis-adducts **9** and **10**. Increase in the size of the ring in the starting diazocycloalkane and in spirohomofullerene as well favored the formation of bis-spiroadducts **11** and **12** with *anti*-arrangement of the attached addends similar to the corresponding bis-methanofullerenes (Scheme 4).

In the mixture of regioisomeric bis-adducts **9** or **10**, the increase in the number of isomers with respect to the arrangement of the substituents in the fullerene core resulted in the increase in the number of the characteristic signals. Thus, the $^{13}$C NMR spectra of regioisomeric mixture of bis-adducts **10** contained multiplets at $\delta_C$ 47—52 (maxima at: $\delta_C$ 48.82, 49.32, 49.58, 49.68, 49.76, 49.95, 50.17, 50.25), 29—32 (maxima at: $\delta_C$ 30.15, 30.58, 30.73, 30.81, 30.89, 31.00, 31.05, 31.18, 31.34), and 37—40 (maxima at: $\delta_C$ 38.70, 38.72, 38.76, 38.95, 39.15, 39.30, 39.32, 39.43, 39.56), which were attributed to the spiro atoms C(2′) and C(6′), and the carbon atoms C(3′)—C(5′), respectively. In the $^1$H NMR spectra of **10**, the number of the signals corresponded to the regioisomeric cycloaddition products is also substantially increased. Thus, the $^1$H NMR spectra exhibited multiplets in the range of $\delta_H$ 1.50—1.85 and 2.00—2.27 for the protons of cyclohexylidene moieties. The mass spectra of the mixture **10** revealed intense peaks for molecular ion with *m/z* 884.863 (calculated 884.929) and fragment ion with *m/z* 802.758 (calculated 802.786) formed by the cleavage of cyclohexylidene moiety from bis-adduct **10**.

In the $^{13}$C NMR spectra of compounds **11** and **12**, the increase in the signal intensities for the carbon atoms, to which the second addends are bounded, with respect to the spectra of the corresponding mono-adducts **3** and **4** was observed. At the same time, a decrease in the number of signals for the sp$^2$-hybridized carbon atoms of the fullerene core was observed suggesting the high symmetry of the resulting bis-adducts **11** and **12** and indicating the *anti*-arrangement of the attached addends.

In summary, it was shown that diazocycloalkanes, which can be generated *in situ* by the oxidation of the corresponding cycloalkanone hydrazones with $MnO_2$, readily underwent selective cycloaddition to [60]fullerene in the presence of a three component catalyst $Pd(acac)_2$—$PPh_3$—$Et_3Al$ to give spirohomofullerenes in fairly yields (70—80%). It was found that the increase in the ring size in the starting diazo compound and in spirohomofullerene as well favored formation of bis-adducts with *anti*-arrangement of the second addends similar to *trans*-1-bis-methanofullerene.

## Experimental

Commercially available [60]fullerene (99.5% pure, G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhniy Novgorod) was used. The reaction products were analyzed using an HPLC chromatograph Altex 330 (USA) equipped with a UV detector (340 nm). The mixtures were separated on semi-preparative column Cosmosil Buckyprep Waters (250×10 mm) at room temperature. Toluene was used as the eluent, the flow rate was 2.0 mL min$^{-1}$. The IR spectra were registered on a Specord 75 IR (Carl Zeiss Jena) spectrophotometer in KBr pellets. The UV spectra were recorded on Specord M-40 and Specord M-80 instrument. The $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance-400 spectrometer at 400.13 and 100.62 MHz, respectively. A mixture of $CDCl_3$ and $CS_2$ (1 : 5) was used as a solvent. The negative-ion mass spectra were obtained on a MALDI TOF/TOF Autoflex-III Bruker mass spectrometer without a matrix operating in a linear mode. Samples were dissolved in toluene prior to application on a metal target.

**Catalytic cycloaddition of generated *in situ* diazocycloalkanes to [60]fullerene (general procedure).** To solutions of $Pd(acac)_2$ (4.2 mg, 0.0139 mmol) in toluene (2 mL) and $PPh_3$ (7.3 mg, 0.0278 mmol) in toluene (2 mL) placed in the glass reactor, a solution of $Et_3Al$ (0.0556 mmol) in toluene (0.3 mL) was added with stirring at −5 °C under argon. The color of the mixture changed from pale yellow to pale brown. To the resulting catalyst, a solution of [60]fullerene (50 mg, 0.0695 mmol) in toluene (50 mL) was added, the color of the mixture turned to dark green. To the resulting fullerene complex, a solution of the corresponding hydrazone (0.104 mmol) in toluene (1 mL) was added followed by portionwise addition of $MnO_2$ (1.0 mmol). After 90 min, the reaction mixture was treated with 5% aqueous HCl and the organic phase was passed through a small layer of silica gel. The reaction products **1—4** and [60]fullerene were separated by semi-preparative HPLC using toluene as the eluent. Thermal isomerization of 5,6-open isomers into 6,6-closed adducts was carried out in accordance with the known procedure.[16,18]

**Spiro[cyclopentane-1,1′a-[1(9)a]homo($C_{60}$-$I_h$)[5,6]fullerene] (1).** IR, ν/cm$^{-1}$: 530, 780, 920, 1080, 1120, 1430. UV ($CHCl_3$), $\lambda_{max}$/nm: 260, 330. $^1$H NMR, δ: 1.69 (t, 2 H, $CH_2$, $^3J$ = 7.2 Hz); 1.85 (quint, 2 H, $CH_2$, $^3J$ = 7.2 Hz); 2.16 (quint, 2 H, $CH_2$, $^3J$ = 7.2 Hz); 3.99 (t, 2 H, $CH_2$, $^3J$ = 7.2 Hz). $^{13}$C NMR, δ: 26.45, 26.57, 35.88, 43.08, 57.49, 137.36 (2 C), 137.95 (2 C), 138.87 (2 C), 138.94 (4 C), 139.48 (2 C), 140.22 (2 C), 141.13 (1 C), 141.39 (2 C), 141.76 (4 C), 141.80 (2 C), 142.30 (4 C), 142.49 (2 C), 142.89 (2 C), 143.00 (2 C), 143.09 (2 C), 143.19 (2 C), 143.43 (6 C), 143.63 (4 C), 143.87 (4 C), 143.99 (4 C), 144.38 (1 C), 144.54 (2 C), 144.84 (1 C), 147.78 (1 C). MS (MALDI-TOF), found: 788.724, calculated for $C_{65}H_8$: 788.759.

**Spiro[cyclohexane-1,1′a-[1(9)a]homo($C_{60}$-$I_h$)[5,6]fullerene] (2).** IR, ν/cm$^{-1}$: 530, 750, 1100, 1220, 1470. UV ($CHCl_3$), $\lambda_{max}$/nm: 264, 336. $^1$H NMR, δ: 1.58 (m, 4 H, 2 $CH_2$); 1.76 (m, 2 H, $CH_2$); 2.18 (m, 2 H, $CH_2$); 3.83 (m, 2 H, $CH_2$). $^{13}$C NMR, δ: 23.48, 24.98, 27.16, 30.96, 39.26, 50.29, 135.06 (2 C), 135.89 (1 C), 136.51 (2 C), 137.82 (2 C), 138.79 (2 C), 138.98 (4 C), 139.55 (2 C), 140.18 (2 C), 141.10 (2 C), 141.53 (2 C), 141.67 (2 C), 141.98 (2 C), 142.00 (2 C), 142.22 (4 C), 142.29 (2 C), 142.76 (2 C), 142.97 (2 C), 143.05 (2 C), 143.23 (1 C), 143.28 (2 C), 143.54 (2 C), 143.70 (2 C), 143.78 (1 C), 143.86 (2 C), 143.99 (2 C), 144.08 (2 C), 144.49 (1 C), 144.90 (2 C), 145.25 (2 C), 147.56 (2 C). MS (MALDI-TOF), found: 802.720, calculated for $C_{66}H_{10}$: 802.786.

**Spiro[cycloheptane-1,1′a-[1(9)a]homo($C_{60}$-$I_h$)[5,6]fullerene] (3).** IR, ν/cm$^{-1}$: 520, 720, 1220, 1380, 1470. UV ($CHCl_3$), $\lambda_{max}$/nm:

260, 336. $^1$H NMR, δ: 1.62 (m, 2 H, $CH_2$); 1.68 (m, 4 H, 2 $CH_2$); 1.82 (m, 2 H, $CH_2$); 2.28 (m, 2 H, $CH_2$); 4.03 (m, 2 H, $CH_2$). $^{13}$C NMR, δ: 24.40, 26.08, 28.28, 28.70, 34.46, 41.84, 53.37, 135.18 (2 C), 135.97 (1 C), 137.25 (4 C), 137.86 (2 C), 138.71 (1 C), 138.86 (1 C), 139.90 (2 C), 140.31 (2 C), 140.85 (2 C), 141.38 (2 C), 141.67 (2 C), 141.88 (2 C), 142.06 (6 C), 142.35 (2 C), 142.69 (2 C), 142.91 (2 C), 143.17 (6 C), 143.58 (2 C), 143.79 (6 C), 143.97 (2 C), 144.19 (2 C), 144.58 (1 C), 144.89 (2 C), 145.26 (2 C), 147.23 (2 C). MS (MALDI-TOF), found: 816.770, calculated for $C_{67}H_{12}$: 816.812.

**Spiro[cyclooctane-1,1′a-[1(9)a]homo($C_{60}$-$I_h$)[5,6]fullerene] (4).** IR, ν/cm$^{-1}$: 520, 720, 1080, 1120, 1430. UV ($CHCl_3$), $\lambda_{max}$/nm: 260, 330. $^1$H NMR, δ: 1.62 (m, 4 H, 2 $CH_2$); 1.70 (m, 2 H, $CH_2$); 1.77 (m, 2 H, $CH_2$); 1.82 (m, 2 H, $CH_2$); 2.28 (m, 2 H, $CH_2$); 4.07 (m, 2 H, $CH_2$). $^{13}$C NMR, δ: 22.83, 25.25, 26.25, 27.90, 28.57, 30.68, 37.45, 53.59, 135.22 (2 C), 135.83 (1 C), 137.38 (2 C), 137.82 (2 C), 138.60 (2 C), 138.83 (2 C), 139.96 (2 C), 140.28 (2 C), 140.80 (2 C), 141.33 (2 C), 141.74 (2 C), 141.77 (2 C), 142.06 (4 C), 142.14 (2 C), 142.30 (2 C), 142.66 (2 C), 142.89 (2 C), 142.96 (1 C), 143.08 (2 C), 143.13 (2 C), 143.16 (2 C), 143.64 (2 C), 143.77 (2 C), 143.79 (1 C), 143.81 (2 C), 144.00 (2 C), 144.20 (2 C), 144.52 (1 C), 144.86 (2 C), 145.30 (2 C), 147.48 (2 C). MS (MALDI-TOF), found: 830.788, calculated for $C_{68}H_{14}$: 830.839.

**Spiro[cyclopropa[1,9]($C_{60}$-$I_h$)[5,6]fullerene-3′,1″-cyclopentane] (5).** IR, ν/cm$^{-1}$: 510, 720, 1080, 1250, 1430. UV ($CHCl_3$), $\lambda_{max}$/nm: 262, 333, 430. $^1$H NMR, δ: 2.33 (m, 4 H, 2 $CH_2$); 2.91 (m, 4 H, 2 $CH_2$). $^{13}$C NMR, δ: 27.32 (2 C), 32.30 (2 C), 49.05, 82.61 (2 C), 137.11 (4 C), 141.13 (4 C), 141.56 (2 C), 142.26 (4 C), 142.41 (4 C), 143.06 (4 C), 143.21 (4 C), 143.66 (4 C), 144.04 (4 C), 144.53 (2 C), 144.68 (4 C), 144.92 (4 C), 145.11 (4 C), 145.65 (4 C), 148.65 (4 C), 148.77 (2 C). MS (MALDI-TOF), found: 788.719, calculated for $C_{65}H_8$: 788.759.

**Spiro[cyclopropa[1,9]($C_{60}$-$I_h$)[5,6]fullerene-3′,1″-cyclohexane] (6).** IR, ν/cm$^{-1}$: 510, 730, 1080, 1280, 1420. UV ($CHCl_3$), $\lambda_{max}$/nm: 260, 330, 427. $^1$H NMR, δ: 2.02 (m, 2 H, $CH_2$); 2.11 (m, 4 H, 2 $CH_2$); 2.74 (t, 4 H, 2 $CH_2$, $^3J$ = 5.6 Hz). $^{13}$C NMR, δ: 26.07 (2 C), 26.76, 29.31 (2 C), 44.15, 82.30 (2 C), 137.69 (4 C), 141.04 (4 C), 142.24 (2 C), 142.31 (6 C), 143.07 (6 C), 143.20 (4 C), 143.75 (4 C), 144.25 (4 C), 144.36 (2 C), 144.81 (4 C), 144.97 (2 C), 145.13 (4 C), 145.24 (4 C), 145.84 (4 C), 148.28 (4 C). MS (MALDI-TOF), found: 802.762, calculated for $C_{66}H_{10}$: 802.786.

**Spiro[cyclopropa[1,9]($C_{60}$-$I_h$)[5,6]fullerene-3′,1″-cycloheptane] (7).** IR, ν/cm$^{-1}$: 520, 1180, 1410. UV ($CHCl_3$), $\lambda_{max}$/nm: 262, 333, 430. $^1$H NMR, δ: 2.05 (m, 4 H, 2 $CH_2$); 2.17 (m, 4 H, 2 $CH_2$); 2.94 (t, 4 H, 2 $CH_2$, $^3J$ = 6.0 Hz). $^{13}$C NMR, δ: 27.25 (2 C), 28.59 (2 C), 31.79 (2 C), 46.25, 82.40 (2 C), 137.60 (4 C), 140.99 (4 C), 142.21 (4 C), 142.26 (4 C), 143.05 (4 C), 143.11 (4 C), 143.20 (2 C), 143.77 (4 C), 144.22 (4 C), 144.40 (2 C), 144.78 (4 C), 144.99 (2 C), 145.11 (4 C), 145.24 (4 C), 145.72 (4 C), 148.74 (4 C). MS (MALDI-TOF), found: 816.776, calculated for $C_{67}H_{12}$: 816.812.

**Spiro[cyclopropa[1,9]($C_{60}$-$I_h$)[5,6]fullerene-3′,1″-cyclooctane] (8).** IR, ν/cm$^{-1}$: 520, 710, 1070, 1140, 1240, 1420. UV ($CHCl_3$), $\lambda_{max}$/nm: 260, 333, 429. $^1$H NMR, δ: 1.99 (m, 6 H, 3 $CH_2$); 2.20 (m, 4 H, 2 $CH_2$); 2.96 (m, 4 H, 2 $CH_2$). $^{13}$C NMR, δ: 26.11 (2 C), 26.33, 27.48 (2 C), 29.87 (2 C), 46.53, 82.81 (2 C), 137.66 (4 C), 140.92 (4 C), 142.20 (8 C), 143.04 (4 C), 143.08 (4 C), 143.21 (2 C), 143.78 (4 C), 144.21 (4 C), 144.41 (2 C), 144.78 (4 C), 144.99 (2 C), 145.11 (4 C), 145.24 (4 C), 145.70 (4 C), 148.94 (4 C). MS (MALDI-TOF), found: 830.792, calculated for $C_{68}H_{14}$: 830.839.

**Mixture of regioisomeric bis-adducts (9).** IR, ν/cm$^{-1}$: 510, 720, 1090, 1240, 1480. UV ($CHCl_3$), $\lambda_{max}$/nm: 262, 330. $^1$H NMR, δ: 1.55—1.90 (m); 2.05—2.25 (m); 3.65—4.08 (m). $^{13}$C NMR, δ: 26.50, 35.60, 35.67, 35.78, 35.90, 35.96, 36.00, 42.36, 42.55, 42.67, 42.79, 42.90, 43.26, 43.32, 43.43, 56.34, 56.44, 56.59, 56.78, 57.11, 57.19, 132.31, 132.82, 132.95, 134.71, 135.08, 135.51, 135.75, 135.95, 136.66, 137.43, 138.02, 138.21, 139.05, 139.66, 139.87, 140.41, 140.95, 141.14, 141.39, 141.57, 142.12, 142.26, 142.61, 143.16, 143.39, 143.70, 143.88, 144.11, 144.35, 144.86, 144.97, 145.18, 145.54, 145.77, 147.55. MS (MALDI-TOF), found: 856.878, calculated for $C_{70}H_{16}$: 856.876.

**Mixture of regioisomeric bis-adducts (10).** IR, ν/cm$^{-1}$: 510, 720, 1080, 1440, 1480. UV ($CHCl_3$), $\lambda_{max}$/nm: 260, 333. $^1$H NMR, δ: 1.51—1.64 (m); 1.70—1.83 (m); 2.01—2.27 (m); 3.38—4.39 (m). $^{13}$C NMR, δ: 23.53, 27.64, 29.98, 30.15, 30.58, 30.73, 30.81, 30.89, 31.00, 31.03, 31.18, 31.34, 38.70, 38.72, 38.76, 38.95, 39.15, 39.30, 39.32, 39.43, 39.56, 48.82, 49.32, 49.58, 49.68, 49.76, 49.87, 49.95, 50.17, 50.25, 134.61, 134.97, 135.18, 135.64, 135.76, 135.98, 136.28, 136.63, 136.73, 136.81, 137.25, 137.69, 137.79, 138.09, 138.19, 138.45, 138.81, 138.96, 139.24, 139.66, 139.78, 140.02, 140.16, 140.31, 140.48, 140.69, 140.77, 140.96, 141.21, 141.31, 141.67, 142.00, 142.14, 142.21, 142.34, 142.58, 142.82, 142.95, 143.11, 143.42, 143.53, 143.63, 143.79, 143.96, 144.06, 144.14, 144.32, 144.44, 144.55, 144.66, 144.87, 145.30, 145.55, 145.68, 145.78, 145.97, 146.09, 146.22. MS (MALDI-TOF), found: 884.863, calculated for $C_{72}H_{20}$: 884.929.

**Dispiro[cycloheptane-1,1′a-[1(2)a,52(60)a]dihomo($C_{60}$-$I_h$)-[5,6]fullerene-52a,1″-cycloheptane] (11).** IR, ν/cm$^{-1}$: 520, 720, 1220, 1440. UV ($CHCl_3$), $\lambda_{max}$/nm: 262, 336. $^1$H NMR, δ: 1.52 (m, 4 H, 2 $CH_2$); 1.65 (m, 8 H, 4 $CH_2$); 1.80 (m, 4 H, 2 $CH_2$); 2.26 (m, 4 H, 2 $CH_2$); 4.00 (m, 4 H, 2 $CH_2$). $^{13}$C NMR, δ: 24.42, 26.03, 28.29, 28.68, 34.54, 41.72, 53.29, 136.17, 137.63, 138.79, 139.04, 139.69, 139.99, 140.99, 141.29, 142.05, 147.32. MS (MALDI-TOF), found: 912.875, calculated for $C_{74}H_{24}$: 912.982.

**Dispiro[cyclooctane-1,1′a-[1(2)a,52(60)a]dihomo($C_{60}$-$I_h$)-[5,6]fullerene-52a,1″-cyclooctane] (12).** IR, ν/cm$^{-1}$: 520, 720, 1080, 1440, 1480. UV ($CHCl_3$), $\lambda_{max}$/nm: 268, 334. $^1$H NMR, δ: 1.67 (m, 8 H, 4 $CH_2$); 1.72 (m, 4 H, 2 $CH_2$); 1.74 (m, 4 H, 2 $CH_2$); 1.83 (m, 4 H, 2 $CH_2$); 2.26 (m, 4 H, 2 $CH_2$); 4.03 (m, 4 H, 2 $CH_2$). $^{13}$C NMR, δ: 22.91, 25.22, 26.28, 27.99, 28.65, 30.63, 37.44, 53.49, 135.03, 136.82, 137.56, 137.76, 137.92, 138.61, 139.32, 139.58, 139.94, 140.14, 140.63, 141.24, 141.73, 142.01, 142.51, 143.16, 144.43. MS (MALDI-TOF), found: 940.940, calculated for $C_{76}H_{28}$: 941.036.

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