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Unexpected Reactions of [60]Fullerene Involving Tertiary Amines and Insight into the Reaction Mechanisms

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Abstract: Thermal reactions of [60]fullerene with amino acid ester hydrochlorides and triethylamine in *o*-dichlorobenzene at reflux afforded pyrrolidinofullerene derivatives containing the CH_3CH moiety and originating from triethylamine through an unusual C–N bond cleavage. Detailed investigation of these thermal reactions resulted in the discovery of unprecedented reactions between C_{60} and tertiary amines and of reactions of C_{60} with tertiary amines and aldehydes, giving cyclopentafullerene derivatives with high stereoselectivity. Plausible reaction mechanisms for the product formation involving the uncommon C–N bond cleavage of tertiary amines were proposed on the basis of extensive experimental results.

Keywords: [60]fullerene · amino acids · cycloaddition · reaction mechanisms · tertiary amines

Introduction

An impressive number of fullerene derivatives have been synthesized by various functionalization methods,[1] some of them having potential for applications in biology and materials sciences.[2] Functionalization of C_{60} with amino acids and their derivatives in order to prepare biologically and pharmacologically active fullerene compounds is of great appeal to chemists.[3] Amino acids and their derivatives can react with C_{60} through 1,3-dipolar cycloadditions of azomethine ylides formed either by decarboxylation of immonium salts generated from condensations of α-amino acids with aldehydes/ketones or from imines of α-amino acid esters.[4] Alternatively, amino acids and peptides can be tethered to side chains of certain fullerene derivatives.[5] Gan's group has explored direct reactions between amino acid esters and C_{60} induced by photoirradiation and ultrasonification.[6]

We have very recently reported novel reactions of C_{60} with amino acid ester hydrochlorides and CS_2 in the presence of triethylamine (Et_3N), which afford fullerene derivatives containing biologically active amino acid, thioamide, and thiourea units.[7] In continuation of our interest in fullerene chemistry,[7,8] we have recently investigated thermal reactions of C_{60} with amino acid ester hydrochlorides and Et_3N in *o*-dichlorobenzene (ODCB) at reflux, and unexpectedly discovered the incorporation into the fullerene products of a CH_3CH moiety originating from Et_3N through C–N bond cleavage. Here we report these novel thermal reactions. More importantly, detailed investigation of these reactions resulted in our discovery of unprecedented thermal reactions between C_{60} and tertiary amines, and also of reactions of C_{60} with tertiary amines and aldehydes, both affording cyclopentafullerene derivatives with high stereoselectivity. On the basis of further extensive experimental results, we present plausible reaction mechanisms for product formation involving an unusual tertiary amine C–N bond cleavage.

Results and Discussion

In a study of thermal reactions between amino acid ester hydrochlorides and C_{60}, Et_3N was added to the reaction mixtures to remove hydrogen chloride from the amino acid ester hydrochlorides. Unexpectedly, though, reactions of C_{60} with amino acid ester hydrochlorides **1a–c** and Et_3N (1:5:10) in ODCB at 220 °C for 1 h under dark and aerobic

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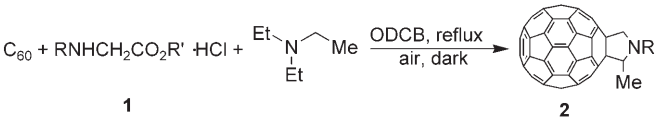
conditions afforded adducts **2a–c** in 34–39% yields (73–79% based on consumed C_{60}) (Scheme 1). The structures of products **2a–c** were unambiguously characterized by their MS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV/Vis spectral data.



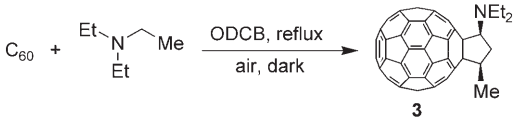
1 **2**

1a, **2a**: R = Me, R' = Et; **1b**, **2b**: R = $PhCH_2$, R' = Et;
1c, **2c**: R = $MeOOCCH_2$, R' = Me

Scheme 1. Synthesis of adducts **2** by the reactions of C_{60} with **1** and Et_3N.

These products are quite different from the corresponding photochemical products,[6] suggesting that the formation of adducts **2a–c** had proceeded by a different pathway (vide infra).

During the work on the reaction of C_{60} with **2c** and Et_3N, it was found that another product (**3**, Scheme 2) was also



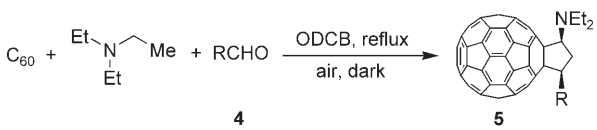
3

Scheme 2. Preparation of adduct **3** by the reaction of C_{60} with Et_3N.

formed when more than 10 equivalents of Et_3N were added. It transpired that product **3** was produced from a direct reaction between C_{60} and Et_3N: treatment of C_{60} and Et_3N (1:100) in ODCB at 220°C for 1 h under dark and aerobic conditions was found to give adduct **3** in 52% yield. The spectral data of adduct **3** were fully consistent with those reported previously.[9]

Adducts **2a–c** and **3** each possessed a common CH_3CH moiety, which might conceivably have originated from Et_3N. We suspected that acetaldehyde might have been generated from the fragmentation/oxidization of Et_3N in ODCB at reflux and might then have participated in a subsequent reaction under our employed conditions. To substantiate our assumption, other aldehydes (RCHO) were added to the reaction mixture of C_{60} and Et_3N to see if products in which the CH_3CH group in adduct **3** had been replaced with the RCH moiety could be obtained. 4-Methoxybenzaldehyde (**4a**) and butyraldehyde (**4b**) were chosen as representative aromatic and aliphatic aldehydes and, much to our satisfaction, treatment of C_{60} with **4a**/**4b** and Et_3N (1:50:100) afforded adducts **5a** (38%)/**5b** (34%) as the major products (Scheme 3), along with minor quantities of adduct **3**.

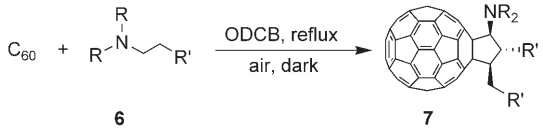
To probe the generality of this type of reaction for other tertiary amines, treatment of C_{60} with tripropylamine (**6a**) and with *N,N*-diisopropylethylamine (**6b**) in place of Et_3N was examined, both in the absence and in the presence of an aldehyde. As desired, treatment of C_{60} with **6a**/**6b** afforded **7a**/**7b** in 31%/18% yield (Scheme 4), whilst treatment of C_{60} with **4a** and **6a**/**6b** resulted in the formation of **8a**/**8b** in



4 **5**

4a, **5a**: R = 4-MeOPh; **4b**, **5b**: R = $CH_3(CH_2)_2$

Scheme 3. Formation of adducts **5** by the reactions of C_{60} with Et_3N and aldehydes **4**.

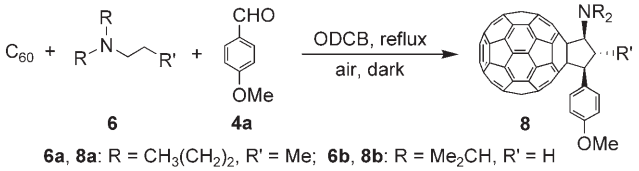


6 **7**

6a, **7a**: R = R = $CH_3(CH_2)_2$, R' = Me; **6b**, **7b**: R = Me_2CH, R' = H

Scheme 4. Formation of adducts **7** by the reactions of C_{60} with tertiary amines **6**.

27%/13% yield (Scheme 5) along with minor quantities of **7a**/**7b**.[10]



6 **4a** **8**

6a, **8a**: R = $CH_3(CH_2)_2$, R' = Me; **6b**, **8b**: R = Me_2CH, R' = H

Scheme 5. Formation of adducts **8** by the reactions of C_{60} with tertiary amines **6** and aldehyde **4a**.

The spectroscopic data for adducts **5a**, **5b**, **7a**, **7b**, **8a**, and **8b** are in agreement with the depicted structures. Notably, compounds **5a**, **5b**, **7b**, and **8b** each exhibited an almost perfect "quartet" at $\delta = 2.7$–3.6 ppm in their ^{1}H NMR spectra, with $J = \approx 12$ Hz, indicating approximately the same geminal and vicinal coupling constants for one of the two nonequivalent methylene protons in the five-membered ring, together with peak broadening at $\delta = 44$–49 ppm (CH_3CH_2N or $(CH_3)_2CHN$) in their ^{13}C NMR spectra, similarly to adduct **3**.[9] Products **5a**, **5b**, **7b**, and **8b** should therefore have *cis* structures, whilst the $(CH_3(CH_2)_2)_2N$ and CH_3 groups in adduct **8a** should be in a *trans* relationship, on the basis of the doublet with $J = 11$ Hz for the C*H*N proton, and the 4-MeOPh and CH_3 groups should also be in a *trans* arrangement, on the basis of the doublet with $J = 12$ Hz for the 4-MeOPhC*H* proton, so the $(CH_3(CH_2)_2)_2N$ and 4-MeOPh groups are also in a *cis* pattern. Similarly, the $(CH_3(CH_2)_2)_2N$ and CH_3CH_2 groups in adduct **7a** are in a *cis* arrangement. These NMR data indicate that all the reactions shown in Scheme 2–5 exhibit very high stereoselectivity and give *cis* products. Many examples of fullerene derivatives with *cis* structures are known in the literature: one example worthy of note is that of bromine, which, while usually adding to an alkene in *trans* fashion, added *cis* to the double bond in the addend of the [60]fullerene–cyclopentadiene adduct to avoid steric hindrance with the fullerene cage.[11]

The *cis* stereochemistries of these cyclopentafullerene derivatives were further supported by the NOESY spectra of the selected compounds **5a**, **7b**, **8a**, and **8b**. The NOEs involving the hydrogens on the cyclopentane ring fused with C_{60} are indicated by the curved arrows in Figure 1. It is obvious that H1 and H4 are in a *cis* relationship in all selected compounds. These NOESY spectra also allow chemical shift assignments of the hydrogens on the cyclopentane ring shown in the Figure 1. It can be seen that the chemical shifts of H1–H4 are almost the same when the $(CH_3CH_2)_2N$ group in **5a** is exchanged for the $((CH_3)_2CH)_2N$ group as in **8b**, while drastic changes in the chemical shifts of H1–H4 are observed when the 4-MeOPh group is replaced with the methyl group (**8b** vs. **7b**) or when one of the methylene hydrogens is changed for a methyl group (**5a** vs. **8a**). The *cis* isomer selectivity of these products can be understood in terms of the bulky NR_2 and 4-MeOPh/Et/Me groups both being able to occupy pseudoequatorial positions in this configuration.

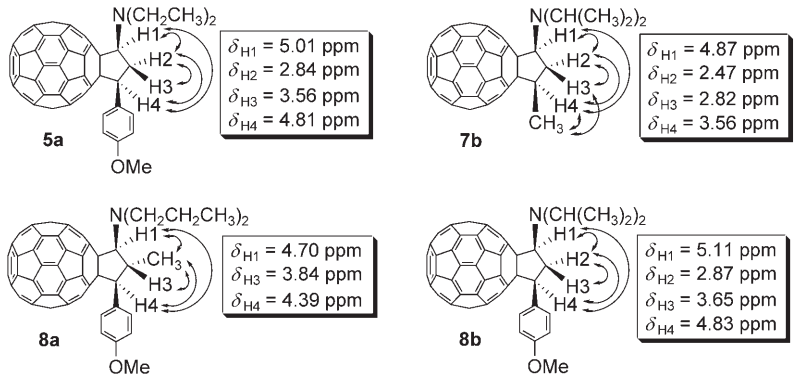
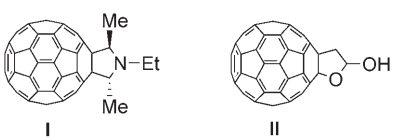


Figure 1. Partial NOEs and chemical shift assignments in compounds **5a**, **7b**, **8a**, and **8b**.

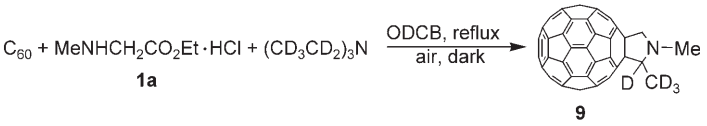
The reaction temperature and the presence of oxygen were found to be critical for product formation in the thermal reactions shown in Schemes 1–5. When, for example, the reaction temperature was decreased to 110 °C, no product could be obtained even after a prolonged reaction time. Strict exclusion of oxygen from the reaction mixtures also resulted in the absence of product formation.

To our surprise, product **3**, obtained from our thermal aerobic reaction between C_{60} and Et_3N, possesses the same structure as that obtained from the anaerobic photochemical reaction between C_{60} and Et_3N, whilst neither adduct **I** nor adduct **II**, the products of air-saturated photochemical reactions between C_{60} and Et_3N,[9] could be isolated from our thermal reaction. The thermal reaction, however, is far superior to the photochemical reaction, for which the reaction mixture had to be deoxygenated and from which adduct **3** was obtained in about a 10% yield based on reacted C_{60}.[9]



In the reactions shown in Scheme 1, adducts **2a–c** could be envisioned as the products of reactions of C_{60} with amino acids and acetaldehyde.[4] Nevertheless, no acetaldehyde had been added to the reaction mixtures. We reasoned that amino acids and acetaldehyde could be formed by the hydrolysis of the acid amino ester hydrochlorides in the presence of Et_3N and by the fragmentation/oxidization of Et_3N, respectively, under our experimental conditions. In fact, control experiments showed that treatment of C_{60} either with *N*-methylglycine and Et_3N (1:1:10) or with *N*-methylglycine and acetaldehyde (1:1:4) in ODCB at 220 °C afforded the same product (**2a**) in 40% and 51% yields, respectively, whereas at 110 °C these reactions gave **2a** in 0% and 44% yields, respectively. These results indicated that the acetaldehyde had not originated from contaminants present in the reagents or solvent, but had indeed resulted from the fragmentation of Et_3N in ODCB at reflux.

Additional evidence for the origination of the CH_3CH moiety from Et_3N through C–N bond cleavage was the observation that the CD_3CD moiety was integrated into the product when $(CD_3CD_2)_3N$ was used to replace Et_3N in the reaction of C_{60} with **1a**, with product **9** being obtained in 32% yield (Scheme 6).

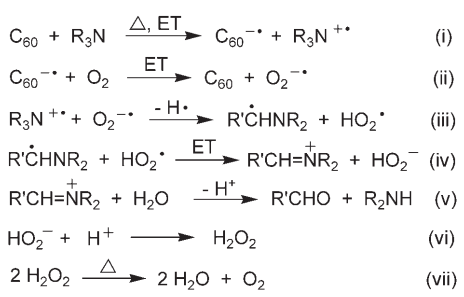


Scheme 6. Synthesis of adduct **9** by the reaction of C_{60} with **1a** and $(CD_3CD_2)_3N$.

In the ^1H NMR spectrum of **9**, the doublet and quartet signals corresponding to the CH_3CH group in **2a** were absent, whilst in its ^{13}C NMR spectrum, the peaks of **9** were almost identical to those of **2a**, except that the peaks at $\delta =$ 72.61 and 16.33 ppm for the CH_3CH group in **2a** were hardly visible, due to the peak broadening arising from the C–D coupling.

Amines are known to transfer single electrons to small organic molecules to give amine cation radicals,[12] and it has been reported that an aldehyde or ketone can be generated from an amine.[12c,13] Primary, secondary and tertiary amines can react with C_{60} to form amine cation radicals and $C_{60}^{-\bullet}$ anion radical.[6,9,14] In most cases the electron transfer between an amine and C_{60} has been initiated photochemical-

ly,[6,9] but there is evidence that amines can transfer single electrons to C_{60} without photoirradiation.[14] Thus, under our high-temperature conditions, a tertiary amine may transfer an electron to C_{60} even in the dark (step i in Scheme 7).[14]

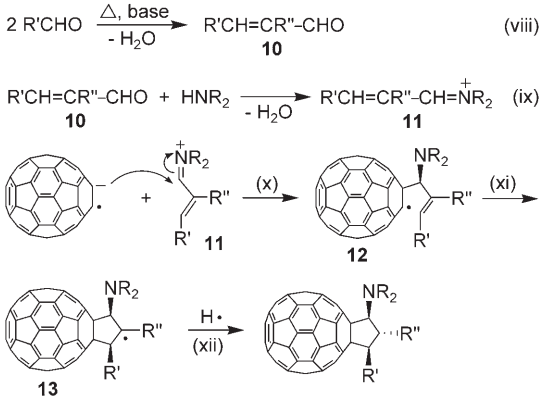


Scheme 7. Proposed aldehyde formation resulting from the C_{60}-mediated C–N bond cleavage of a tertiary amine.

The following steps (steps ii–v) for C_{60}-mediated aldehyde formation from a tertiary amine are also shown in Scheme 7. Anion radical $C_{60}^{-\bullet}$ reduces molecular oxygen to generate neutral C_{60} and superoxide anion $O_2^{-\bullet}$ (step ii).[14c] Deprotonation of the methylene carbon α to the amine cation radical by $O_2^{-\bullet}$ gives neutral radicals $R'(NR_2)CH^{\bullet}$ and $HO_2^{\bullet}$ (step iii),[15] followed by electron transfer between the last two radicals to form iminium cation $R'CH{=}N^+R_2$ and HO_2^- (step iv).[13b] Alternatively, $O_2^{-\bullet}$ may directly abstract a hydrogen from the methylene group α to the nitrogen atom of the amine cation radical to afford $R'CH{=}N^+R_2$ and HO_2^-. Hydrolysis of the imine cation $R'CH{=}N^+R_2$ to produce aldehyde R′CHO (step v) is a well-known process.[13]

By the mechanism shown in Scheme 7, Et_3N would afford acetaldehyde. A similar reaction pathway has been proposed to explain the formation of acetaldehyde and diethylamine from Et_3N in situ on initiation by single-electron transfer.[13a] Once acetaldehyde is generated, it reacts with the amino acids formed from the hydrolysis of the corresponding amino acid ester hydrochlorides to give the azomethine ylides, which then undergo [2+3] cycloaddition reactions with C_{60}. The initially unexpected products **2a–c** in Scheme 1 could thus be attributed to the well-known Prato reaction.[4]

The photochemical reactions between tertiary amines and C_{60} to give pyrrolidinofullerene derivatives take place at the two carbons α to the nitrogen atom, accompanied by two C–H bond cleavages.[9,15] The formation of cyclopentafullerene derivatives **3**, **7a**, and **7b**, however, requires the participation of two molecules of tertiary amines, while that of **5a**, **5b**, **8a**, and **8b** involves the fusion of C_{60} with one molecule of aldehyde and one molecule of tertiary amine, the reactions apparently occurring at both α- and β-carbon atoms of the same alkyl group of the tertiary amine. These seemingly different reactions in fact proceed by the same reaction mechanism, as formulated in Scheme 8. Condensation of two molecules of the formed aldehyde R′CHO (from step v) generates α,β-unsaturated aldehyde **10** (step viii), which

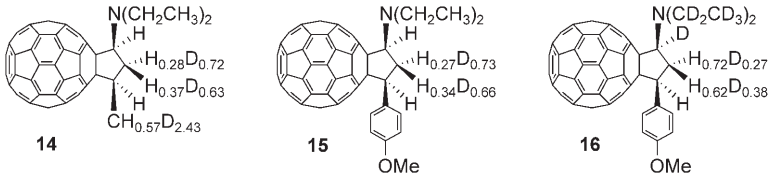


Scheme 8. Proposed reaction mechanism for the formation of cyclopentafullerene derivatives.

reacts with the formed secondary amine to give iminium cation **11** (step ix). $C_{60}^{-\bullet}$, formed by electron transfer either from the generated secondary amine or from the original tertiary amine, reacts with **11** to afford fullerene radical **12**. Intramolecular cyclization (step xi) of **12** and subsequent hydrogen abstraction (step xii) preferentially give the *cis* products **3**, **7a**, and **7b**.[16] Alternatively, fullerene radical **12** could be formed by reaction between C_{60} and the radical $R'CH{=}CR''{-}CH{-}NR_2^{\bullet}$ radical, generated from iminium cation **11** by electron transfer from either $C_{60}^{-\bullet}$ or $O_2^{-\bullet}$. When the formed aldehyde reacts with one molecule of another deliberately added aldehyde, the final products will be the *cis* compounds **5a**, **5b**, **8a**, and **8b**.

It should be noted that both acetaldehyde and acetone could be generated from **6b** in the reaction mechanism shown in Scheme 7, but no product resulting from the participation of acetone in the reaction between C_{60} and **6b** could be identified. The reason might be less favourable formation of α,β-unsaturated carbonyl compound **10** with acetone than with acetaldehyde (step viii).

Further insight into the proposed mechanism was provided by isotope experiments. Interestingly, deuterium was incorporated into the products (**14** and **15**) when D_2O was added to the reaction mixture of C_{60}, Et_3N, and **4a**. Products **14** and **15** were in fact both mixtures consisting of compounds with different numbers of hydrogen and deuterium atoms at the methylene and methyl groups, and the ratios of hydrogen and deuterium atoms in products **14** and **15** were



determined from the integrals in their ^{1}H NMR spectra. Deuterium atoms could be found at both upward and downward positions in the methylene group, strongly suggesting a deuterium abstraction process from both sides of radical **13**. The slight overpopulation of deuterium at the position *trans* to the NEt_2 and Me/4-MeOPh groups was genuine, as confirmed by several independent experiments, and probably due to the smaller steric hindrance encountered by D_2O from the direction *trans* to the bulkier groups. The total number of both hydrogen and deuterium atoms of the methylene group should be unity if it were assumed that no deuterium–hydrogen exchange occurred. The observed 35–39% excess of deuterium at the methylene group could be understood in terms of deuterium–hydrogen exchange at the CH_3 group of acetaldehyde in the presence of a base, thus resulting in partial deuterium substitution of the hydrogen ($R'' = H$) in **10** and **11**. The same deuterium–hydrogen exchange at the CH_3 group of acetaldehyde also resulted in partial deuterium substitution at the methyl group ($R' = CH_3$) in **10** and **11**, and further allylic deuterium–hydrogen exchange in **10** and **11** could explain why more hydrogen atoms of the methyl group were substituted by deuterium atoms (81%) in product **14**. The proposed mechanism shown in Scheme 8 is also consistent with the incorporation of deuterium atom only at the methylene and methyl groups of **14** and **15**, while the two methine groups remain unchanged. In addition, a reversal of the H/D distribution relative to product **15** was observed in product **16**, which was synthesized by the reaction of C_{60} with $(CD_3CD_2)_3N$ and **4a** in the presence of adventitious and formed H_2O. All these deuterium experiments support our proposed mechanism.

Control experiments showed that the reaction of C_{60} with diethylamine and acetaldehyde (1:20:40) produced **3** in 23% yield, while the reaction of C_{60} with diethylamine, acetaldehyde, and **4a** (1:50:50:50) gave both **3** and **5a** in 11 and 10% yields, respectively. These experimental results further validate our proposed mechanism.

To date, few fullerene derivatives fused with full-carbon five-membered rings are known.[16,17] These reactions between C_{60} and tertiary amines, either in the absence or in the presence of an aldehyde, are novel ways to construct fullerene derivatives fused with full-carbon five-membered rings. The reaction between a tertiary amine and an alkene—as well as the reaction of a tertiary amine with an alkene and an aldehyde—to afford a cyclopentane derivative have no precedent.

Conclusion

We have discovered a novel route for the preparation of cyclopentafullerene derivatives involving quite unexpected thermal reactions of tertiary amines in ODCB at reflux, and we have proposed possible reaction mechanisms based on extensive experiments. Products **3**, **5a**, **5b**, **7a**, **7b**, **8a**, and **8b** each bear an amino group, which could be transformable to provide water-soluble quaternary ammonium salts of C_{60}. It is anticipated that these amphiphilic fullerenes may have potential applications in biology and materials sciences.[2] Work along this line and further applications of reactions of C_{60} with a tertiary/secondary amine and an aldehyde are currently under investigation.

Experimental Section

General methods: ^{1}H and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, in $CS_2/CDCl_3$, CS_2/C_6D_6 or $CS_2/[D_6]DMSO$, chemical shifts (δ) are given in ppm relative to solvents, and coupling constants (J) are given in Hz. MALDI-TOF mass spectra were taken on a Bruker BiFlexIII mass spectrometer with 4-hydroxy-α-cyanocinnamic acid as the matrix, and FAB mass spectra were obtained on a VG ZAB-HS mass spectrometer with 3-nitrobenzyl alcohol as the matrix. IR spectra were recorded on a Shimadzu 8600 FT IR spectrometer. UV/Vis spectra were obtained on a Shimadzu UV-2100 PC spectrometer. Chromatographic purifications were carried out with 200–300 mesh silica gel. C_{60} (>99.9%) was purchased from Henan Tian'an Company, China. All other commercial available reagents are of analytical grade.

1′,2′-Dimethyl-pyrrolidino[3′,4′:1,9](C$_{60}$-*I*$_h$)[5,6]fullerene (2a): A 25-mL round-bottomed flask containing a mixture of C_{60} (36.0 mg, 0.05 mmol), sarcosine ethyl ester hydrochloride (**1a**, 38.5 mg, 0.25 mmol) and Et_3N (70 μL, 0.50 mmol) in ODCB (10 mL) was wrapped in aluminum foil and heated in an oil bath preset at 220 °C for 1 h. After removal of the solvent in vacuo, flash chromatography of the residue on a silica gel column, with carbon disulfide and then toluene as the eluent, afforded unreacted C_{60} (17.3 mg, 48%) and adduct **2a** (15.4 mg, 39%). ^{1}H NMR (300 MHz, $CS_2/CDCl_3$): δ = 4.79 (d, J_{ab} = 9.3 Hz, 1H), 4.08 (d, J_{ab} = 9.3 Hz, 1H), 3.88 (q, J = 6.3 Hz, 1H), 2.90 (s, 3H), 1.96 (d, J = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent, all 1C unless indicated): δ = 155.56, 153.48, 153.24, 152.37, 146.59 (2C), 146.04, 145.95, 145.82, 145.65, 145.61, 145.50 (2C), 145.43, 145.41, 145.29 (2C), 145.11, 144.84 (4C), 144.71, 144.62 (3C), 144.57, 144.51, 144.08, 143.96, 143.71 (2C), 142.49, 142.37, 142.02, 141.98, 141.94 (2C), 141.57, 141.54, 141.51, 141.48 (2C), 141.40 (2C), 141.38 (2C), 141.27, 141.06, 141.02, 139.60, 139.51 (2C), 139.13, 136.77, 135.73, 135.27, 135.06, 75.31 (sp^3-*C* of C_{60}), 72.61 (*C*HCH$_3$), 69.61 (*C*H$_2$), 68.56 (sp^3-*C* of C_{60}), 38.90 (N*C*H$_3$), 16.33 (CH*C*H$_3$) ppm; FT-IR (KBr): $\tilde{\nu}$ = 2920, 2851, 2772, 1510, 1461, 1426, 1376, 1331, 1186, 766, 574, 526 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} = 256, 304, 430, 702 nm; MS(MALDI-TOF): *m/z*: 791 $[M]^-$.

1′-Benzyl-2′-methylpyrrolidino[3′,4′:1,9](C$_{60}$-*I*$_h$)[5,6]fullerene (2b): This compound was prepared as described for **2a**, from C_{60} (36.0 mg, 0.05 mmol), *N*-benzylglycine ethyl ester hydrochloride (**1b**, 57.5 mg, 0.25 mmol) and Et_3N (70 μL, 0.50 mmol). Yield = 14.9 mg, 34%. Recovered C_{60}: yield = 20.5 mg, 57%. ^{1}H NMR (300 MHz, $CS_2/CDCl_3$): δ = 7.66 (d, J = 7.2 Hz, 2H), 7.44 (t, J = 7.4 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 4.68 (d, J_{ab} = 13.1 Hz, 1H), 4.64 (d, J_{ab} = 9.4 Hz, 1H), 4.17 (q, J = 6.3 Hz, 1H), 3.97 (d, J_{ab} = 9.4 Hz, 1H), 3.76 (d, J_{ab} = 13.1 Hz, 1H), 2.06 (d, J = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent, all 1C unless indicated): δ = 155.70, 153.59, 153.23, 152.45, 146.57 (2C), 146.12, 145.99, 145.77, 145.64, 145.57, 145.49, 145.45, 145.41, 145.36, 145.27 (2C), 145.09, 144.91, 144.82 (2C), 144.76, 144.70, 144.58 (3C), 144.53, 144.47, 144.07, 143.95, 143.71, 143.68, 142.46, 142.33, 141.98, 141.95, 141.93, 141.89, 141.61, 141.51 (2C), 141.45 (2C), 141.40, 141.34 (3C), 141.22, 140.99 (2C), 139.53, 139.46 (2C), 139.04, 137.35 (aryl *C*), 136.82, 135.69, 135.35, 135.03, 128.26 (2C, aryl *C*), 128.12 (2C, aryl *C*), 126.96 (aryl *C*), 75.05 (sp^3-*C* of C_{60}), 70.58 (*C*HCH$_3$), 68.29 (sp^3-*C* of C_{60}), 66.25 (*C*H$_2$), 55.86 (N*C*H$_2$), 16.65 (CH*C*H$_3$) ppm; FT-IR (KBr): $\tilde{\nu}$ = 2923, 2853, 2787, 1452, 1428, 1378, 1334, 1185, 736, 697, 574, 527 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} = 257, 305, 430, 701 nm; MS(FAB): *m/z*: 868 $[M+1]^+$.

1′-Methoxycarbonylmethyl-2′-methylpyrrolidino[3′,4′:1,9](C$_{60}$-*I*$_h$)-[5,6]fullerene (2c): This compound was prepared as described for **2a**, from C_{60} (36.0 mg, 0.05 mmol), dimethyl iminodiacetate hydrochloride

(**1c**, 49.5 mg, 0.25 mmol) and Et_3N (70 μL, 0.50 mmol). Yield = 14.7 mg, 35%. Recovered C_{60}: yield = 18.7 mg, 52%. ^{1}H NMR (300 MHz, CS_2/$CDCl_3$): δ = 4.94 (d, J_{ab} = 9.2 Hz, 1H), 4.49 (d, J_{ab} = 9.2 Hz, 1H), 4.49 (q, J = 6.4 Hz, 1H), 4.15 (d, J_{ab} = 16.7 Hz, 1H), 3.88 (s, 3H), 3.86 (d, J_{ab} = 16.6 Hz, 1H), 1.96 (d, J = 6.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CS_2/$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated): δ = 169.52 (*C*OO), 155.68, 153.42, 153.15, 152.23, 146.77, 146.75, 146.17, 146.04, 145.94, 145.82, 145.77, 145.67 (2C), 145.59, 145.57, 145.45 (2C), 145.25, 145.00 (4C), 144.90, 144.81, 144.77 (2C), 144.72, 144.67, 144.26, 144.10, 143.88, 143.86, 142.64, 142.52, 142.18, 142.14, 142.09 (2C), 141.75, 141.69, 141.65 (3C), 141.55 (2C), 141.52 (2C), 141.41, 141.21, 141.16, 139.75, 139.66 (2C), 139.22, 137.12, 135.89, 135.59, 135.34, 74.67 (sp^3-*C* of C_{60}), 68.74 (*C*HCH$_3$), 68.63 (sp^3-*C* of C_{60}), 65.69 (*C*H$_2$), 51.24 (*C*H$_2$COOCH$_3$), 51.10 (CH$_2$COO*C*H$_3$), 16.14 (CH*C*H$_3$) ppm; FT-IR (KBr): $\tilde{\nu}$ = 2921, 2851, 1736, 1510, 1461, 1428, 1378, 1188, 1169, 766, 574, 526 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} = 256, 307, 430, 702 nm; MS(FAB): *m/z*: 850 $[M+1]^+$.

***cis*-3′-(*N*,*N*-Diethylamino)-5′-methylcyclopenta[1′,2′:1,9](C$_{60}$-*I*$_h$)-[5,6]fullerene (3):** A 25-mL round-bottomed flask charged with a solution of C_{60} (36.0 mg, 0.05 mmol) and Et_3N (697 μL, 5.00 mmol) in ODCB (10 mL) was wrapped with aluminum foil and heated in an oil bath preset at 220°C for 1 h. After conventional workup, flash chromatography on a silica gel column with carbon disulfide as the eluent afforded unreacted C_{60} (7.9 mg, 22%) and adduct **3** (22.2 mg, 52%).

***cis*-3′-(*N*,*N*-Diethylamino)-5′-(4-methoxyphenyl)cyclopenta[1′,2′:1,9](C$_{60}$-*I*$_h$)[5,6]fullerene (5a)**: This compound was prepared as described for **3**, from C_{60} (36.0 mg, 0.05 mmol), Et_3N (697 μL, 5.00 mmol) and 4-methoxybenzaldehyde (**4a**, 304 μL, 2.50 mmol) for 15 min. Yield = 17.7 mg, 38%. **3**: yield = 1.7 mg, 4%. Recovered C_{60}: yield = 15.5 mg, 43%. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$): δ = 7.50 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 5.01 (dd, J = 12.6, 4.5 Hz, 1H), 4.81 (dd, J = 13.5, 4.5 Hz, 1H), 3.75 (s, 3H), 3.56 (q, J = 12.6 Hz, 1H), 3.26–3.18 (m, 2H), 3.11–3.02 (m, 2H), 2.84 (dt, J = 11.8, 4.5 Hz, 1H), 1.16 (t, J = 7.0 Hz, 6H) ppm; ^{13}C NMR (75 MHz, CS_2/$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated): δ = 158.26 (aryl *C*), 156.35, 155.81, 154.11, 153.90, 147.22, 146.88, 146.53, 146.36, 145.90, 145.57, 145.53 (2C), 145.44 (2C), 145.34, 145.30, 145.20, 145.14, 145.05, 144.91, 144.65, 144.55, 144.50 (3C), 144.40 (2C), 144.27, 143.91, 143.80, 143.71, 143.62, 142.45, 142.30, 141.93, 141.90, 141.87, 141.79, 141.70, 141.59, 141.56, 141.47, 141.44, 141.31, 141.26, 141.08, 141.07, 141.03, 140.99, 140.87, 139.34, 138.83, 138.78, 138.63, 135.29, 134.93, 134.12, 133.49, 129.58 (2C, aryl *C*), 129.03 (aryl *C*), 113.41 (2C, aryl *C*), 75.82 (N*C*H), 75.51 (sp^3-*C* of C_{60}), 74.46 (sp^3-*C* of C_{60}), 56.06 (*C*HAr), 54.45 (O*C*H$_3$), 45.00 (br, N*C*H$_2$CH$_3$), 31.42 (CH*C*H$_2$CH), 13.58 (NCH$_2$*C*H$_3$) ppm; FT-IR (KBr): $\tilde{\nu}$ = 2961, 2924, 2853, 1613, 1513, 1462, 1428, 1380, 1252, 1178, 1109, 1067, 1039, 826, 574, 527 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} = 256, 309, 430, 707 nm; MS(MALDI-TOF): *m/z*: 939 $[M]^-$.

***cis*-3′-(*N*,*N*-Diethylamino)-5′-propylcyclopenta[1′,2′:1,9](C$_{60}$-*I*$_h$)-[5,6]fullerene (5b)**: This compound was prepared as described for **3**, from C_{60} (36.0 mg, 0.05 mmol), Et_3N (697 μL, 5.00 mmol) and butyraldehyde (**4b**, 225 μL, 2.50 mmol) for 45 min. Yield = 14.9 mg, 34%. Compound **3**: yield = 4.2 mg, 10%. Recovered C_{60}: yield = 13.3 mg, 37%. ^{1}H NMR (300 MHz, CS_2/$CDCl_3$): δ = 4.85 (dd, J = 12.4, 5.0 Hz, 1H), 3.64–3.53 (m, 1H), 3.18–3.06 (m, 2H), 3.02–2.91 (m, 2H), 2.86–2.79 (m, 1H), 2.73 (q, J = 12.2 Hz, 1H), 2.60–2.49 (m, 1H), 2.04–1.82 (m, 2H), 1.81–1.63 (m, 1H), 1.14 (t, J = 7.3 Hz, 6H), 1.12 (t, J = 7.5 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CS_2/$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated): δ = 156.70, 156.25, 154.02, 153.90, 147.34, 146.72, 146.36, 146.15, 145.78, 145.62, 145.40, 145.32, 145.25, 145.19, 145.15, 145.07, 145.03, 145.01, 144.93, 144.75, 144.43, 144.36 (2C), 144.32, 144.24 (2C), 144.14, 144.11, 143.78, 143.64, 143.57, 143.40, 142.32, 142.16, 141.74 (2C), 141.68 (2C), 141.55, 141.47, 141.35, 141.30, 141.26, 141.18, 141.04, 140.99, 140.91, 140.82, 140.79, 140.74, 139.14, 138.81, 138.66, 138.51, 135.34, 134.66, 134.05, 133.13, 75.97 (sp^3-*C* of C_{60}), 75.69 (N*C*H), 72.96 (sp^3-*C* of C_{60}), 50.47 (*C*HCH$_2$CH$_2$CH$_3$), 44.81 (br, N*C*H$_2$CH$_3$), 34.56 (CH*C*H$_2$CH$_2$CH$_3$), 31.30 (CH*C*H$_2$CH), 21.93 (CHCH$_2$*C*H$_2$CH$_3$), 13.97 (CHCH$_2$CH$_2$*C*H$_3$), 13.46 (NCH$_2$*C*H$_3$) ppm; FT-IR (KBr): $\tilde{\nu}$ = 2954, 2921, 2852, 1513, 1461, 1427, 1378, 1212, 1179, 1108, 1075, 1025, 574, 527 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} = 256, 319, 430, 709 nm; MS(MALDI-TOF): *m/z*: 875 $[M]^-$.

***cis*-3′-Ethyl-4′-methyl-5′-(*N*,*N*-dipropylamino)cyclopenta[1′,2′:1,9](C$_{60}$-*I*$_h$)-[5,6]fullerene (7a)**: A 50-mL round-bottomed flask charged with a solution of C_{60} (50.4 mg, 0.07 mmol) and tripropylamine (**6a**, 334 μL, 1.75 mmol) in ODCB (15 mL) was wrapped in aluminum foil and heated in an oil bath preset at 220°C for 2 h. After the solvent had been removed in vacuo, flash chromatography of the residue on a silica gel column, with carbon disulfide as the eluent, gave a fraction (32.2 mg) that contained C_{60} and **7a**. The percentages of C_{60} and **7a** were 25% and 61%, respectively, based on the HPLC integrals of C_{60} and **7a** on a Buckyprep column (4.6 mm × 250 mm) with toluene/petroleum ether (1:1) as the eluent and detection wavelength at 326 nm, so the fraction contained 8.1 mg of C_{60} (16%) and 19.6 mg of **7a** (31%) (the estimations by HPLC integrals may be slightly different from the actual values due to slightly different extinction coefficients of C_{60} and its derivative at 326 nm; the same applies to the other estimations based on HPLC integrals). Pure **7a** was obtained by HPLC separation of the flash chromatographic fraction on the Buckyprep column, with toluene/petroleum ether (1:1) as the eluent. ^{1}H NMR (300 MHz, CS_2/C_6D_6): δ = 4.45 (d, J = 10.9 Hz, 1H), 3.22–2.89 (m, 6H), 2.52–2.38 (m, 1H), 2.29–2.15 (m, 1H), 1.63–1.41 (m, 2H), 1.56 (d, J = 5.8 Hz, 3H), 1.35 (t, J = 7.5 Hz, 3H), 1.30–1.15 (m, 1H), 0.87 (t, J = 7.3 Hz, 3H), 0.78 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CS_2/C_6D_6 with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated): δ = 158.02, 158.00, 155.46, 155.39, 148.42, 147.74, 147.50, 147.28, 146.98, 146.71, 146.59, 146.52, 146.45, 146.39, 146.34, 146.27, 146.25, 146.22, 146.13, 146.02, 145.61, 145.57, 145.53 (2C), 145.41 (2C), 145.29, 145.27, 144.99, 144.83, 144.73, 144.62, 143.56, 143.38, 142.97 (2C), 142.93, 142.91, 142.60 (2C), 142.56, 142.49, 142.46, 142.37, 142.20, 142.13, 142.04, 142.03, 142.00, 141.85, 140.26, 139.82 (2C), 139.67, 136.61, 135.80, 135.11, 134.23, 82.80 (N*C*H), 76.41 (sp^3-*C* of C_{60}), 74.17 (sp^3-*C* of C_{60}), 58.62 (*C*HCH$_2$CH$_3$), 58.13 (NCH$_2$CH$_2$CH$_3$), 52.44 (NCH$_2$CH$_2$CH$_3$), 40.55 (*C*HCH$_3$), 24.45 (NCH$_2$*C*H$_2$CH$_3$), 24.23 (NCH$_2$*C*H$_2$CH$_3$), 23.93 (CH*C*H$_2$CH$_3$), 17.57 (CH*C*H$_3$), 14.35 (CHCH$_2$*C*H$_3$), 12.45 (NCH$_2$CH$_2$*C*H$_3$), 12.33 (NCH$_2$CH$_2$*C*H$_3$) ppm; FT-IR (KBr): $\tilde{\nu}$ = 2956, 2925, 2868, 1462, 1428, 1378, 1203, 1188, 1078, 574, 527 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} = 255, 321, 430, 713 nm; MS(MALDI-TOF): *m/z*: 904 $[M+1]^+$.

***cis*-3′-(*N*,*N*-Diisopropylamino)-5′-methylcyclopenta[1′,2′:1,9](C$_{60}$-*I*$_h$)-[5,6]fullerene (7b)**: This compound was prepared as described for **7a**, from C_{60} (50.4 mg, 0.07 mmol) and *N*,*N*-diisopropylethylamine (**6b**, 300 μL, 1.75 mmol) at 180°C for 20 min. Flash chromatography afforded a fraction (25.8 mg) that contained C_{60} and **7b**. The percentages of C_{60} and **7b** were 34% and 43%, respectively, based on the HPLC integrals of C_{60} and **7b**, so the fraction contained 8.8 mg of C_{60} (17%) and 11.1 mg of **7b** (18%). Further elution with carbon disulfide gave 3.9 mg of a pure product (I), the structure of which was similar to **7b**, but has not yet been assigned. Pure **7b** was obtained by HPLC separation on the Buckyprep column, with toluene/petroleum ether (1:1) as the eluent. ^{1}H NMR (300 MHz, CS_2/C_6D_6): δ = 4.87 (dd, J = 12.7, 4.6 Hz, 1H), 3.75–3.66 (m, 1H), 3.62–3.49 (m, 1H), 3.30–3.21 (m, 1H), 2.82 (q, J = 12.4 Hz, 1H), 2.47 (dt, J = 11.8, 4.7 Hz, 1H), 1.76 (d, J = 6.8 Hz, 3H), 1.24 (d, J = 6.3 Hz, 3H), 1.19 (d, J = 6.4 Hz, 3H), 1.07 (d, J = 6.7 Hz, 3H), 0.93 (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CS_2/C_6D_6 with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated): δ = 157.91, 157.87, 155.43, 154.83, 148.48, 147.92, 147.52, 147.30, 146.85, 146.64, 146.59, 146.50, 146.43, 146.41, 146.35, 146.24 (2C), 146.19, 146.08, 145.93, 145.64, 145.62, 145.57, 145.49, 145.42, 145.37, 145.32, 145.27, 144.93, 144.82, 144.73, 144.61, 143.53, 143.39, 142.97, 142.95, 142.91, 142.89, 142.74, 142.70, 142.54, 142.49, 142.44, 142.37, 142.21, 142.17, 142.14, 142.06, 142.03, 141.82, 140.17, 140.13, 139.85, 139.77, 136.84, 135.78, 135.05, 134.17, 77.40 (sp^3-*C* of C_{60}), 74.10 (sp^3-*C* of C_{60}), 71.48 (N*C*HCH$_2$), 48.87 (br, N*C*H-(CH$_3$)$_2$), 45.95 (CH$_2$*C*HCH$_3$), 45.06 (br, N*C*H(CH$_3$)$_2$), 38.76 (CH*C*H$_2$CH), 25.86 (br, NCH(*C*H$_3$)$_2$), 23.23 (br, NCH(*C*H$_3$)$_2$), 22.21 (br, NCH(*C*H$_3$)$_2$), 21.73 (br, NCH(*C*H$_3$)$_2$), 17.97 (CH$_2$CH*C*H$_3$) ppm; FT-IR (KBr): $\tilde{\nu}$ = 2957, 2923, 2855, 1514, 1460, 1427, 1393, 1361, 1215, 1186, 1152, 1121, 1080, 575, 527 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} = 256, 326, 429, 715 nm; MS(MALDI-TOF): *m/z*: 862 $[M+1]^+$.

***cis*-3′-(4-Methoxyphenyl)-4′-methyl-5′-(*N*,*N*-dipropylamino)cyclopenta[1′,2′:1,9](C$_{60}$-*I*$_h$)[5,6]fullerene (8a)**: This compound was prepared as described for **7a**, from C_{60} (50.4 mg, 0.07 mmol), **6a** (334 μL, 1.75 mmol) and **4a** (426 μL, 3.50 mmol) for 1 h. Flash chromatography afforded a fraction (25.0 mg) that contained C_{60} and **7a**. The percentages of C_{60} and **7a** were 52% and 31%, respectively, based on the HPLC integrals of C_{60} and **7a**, so the fraction contained 13.0 mg of C_{60} (26%) and 7.8 mg of **7a** (12%). Further elution with carbon disulfide gave 18.8 mg of **8a** (27%). Pure **8a** for spectral characterization was obtained by further flash chromatographic separation on a silica gel column with carbon disulfide as the eluent and by cutting off the first part of the fraction band. ^{1}H NMR (300 MHz, CS_2/[D$_6$]DMSO): δ = 7.50 (d, J = 7.9 Hz, 1H), 7.32 (d, J = 8.2 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 6.75 (d, J = 8.3 Hz, 1H), 4.70 (d, J = 11.3 Hz, 1H), 4.39 (d, J = 12.2 Hz, 1H), 3.91–3.76 (m, 1H), 3.71 (s, 3H), 3.29–3.20 (m, 1H), 3.17–2.94 (m, 3H), 1.73–1.53 (m, 2H), 1.47 (d, J = 6.2 Hz, 3H), 1.34–1.22 (m, 1H), 0.91 (t, J = 7.3 Hz, 3H), 0.83 (t, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CS_2/[D$_6$]DMSO with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated): δ = 157.90 (aryl *C*), 156.46, 155.96, 154.25, 154.19, 147.01, 146.53, 146.10, 145.95, 145.51, 145.45, 145.13, 145.12, 145.02 (2C), 144.97, 144.91, 144.81, 144.76, 144.74, 144.61, 144.24, 144.12 (2C), 144.07, 144.06, 143.98 (2C), 143.88, 143.56, 143.42, 143.36, 143.29, 142.08, 141.92, 141.55, 141.52, 141.47, 141.40, 141.33, 141.17, 141.16, 141.08, 141.05, 140.92, 140.82, 140.72, 140.69, 140.67, 140.60, 140.52, 138.85, 138.50, 138.35, 138.25, 134.95, 134.68, 133.63, 133.20, 132.06 (br, aryl *C*), 127.63 (aryl *C*), 127.56 (br, aryl *C*), 113.92 (br, aryl *C*), 112.62 (br, aryl *C*), 81.09 (N*C*H), 74.63 (sp^3-*C* of C_{60}), 74.15 (sp^3-*C* of C_{60}), 62.28 (*C*HAr), 56.63 (N*C*H$_2$CH$_2$CH$_3$), 54.00 (O*C*H$_3$), 51.16 (NCH$_2$*C*H$_2$CH$_3$), 38.14 (*C*HCH$_3$), 23.02 (NCH$_2$*C*H$_2$CH$_3$), 22.96 (NCH$_2$*C*H$_2$CH$_3$), 15.70 (CH*C*H$_3$), 11.29 (NCH$_2$CH$_2$*C*H$_3$), 11.19 (NCH$_2$CH$_2$*C*H$_3$) ppm; FT-IR (KBr): $\tilde{\nu}$ = 2955, 2925, 2867, 1610, 1512, 1461, 1427, 1375, 1304, 1249, 1204, 1178, 1078, 1037, 827, 573, 527 cm^{-1}; UV/Vis (CHCl$_3$): λ_{max} = 255, 316, 430, 712 nm; MS(MALDI-TOF): m/z: 982 $[M+1]^+$.

***cis*-3′-(*N*,*N*-Diisopropylamino)-5′-(4-methoxyphenyl)cyclopenta[1′,2′:1,9](C$_{60}$-*I*$_h$)[5,6]fullerene (8b)**: This compound was prepared as described for **7a**, from C_{60} (50.4 mg, 0.07 mmol), **6b** (300 μL, 1.75 mmol) and **4a** (426 μL, 3.50 mmol) at 180°C for 15 min. Flash chromatography afforded a fraction (22.7 mg) that contained C_{60} and **7b**. The percentages of C_{60} and **7b** were 72% and 8%, respectively, based on the HPLC integrals, so the fraction contained 16.3 mg of C_{60} (32%) and 1.8 mg of **7b** (3%). Further elution with carbon disulfide gave 1.3 mg of product (I), 8.8 mg of **8b** (13%), and 5.6 mg of another pure product (II), the structure of which was similar to **8b**, but has not yet been assigned. ^{1}H NMR (300 MHz, CS_2/$CDCl_3$): δ = 7.51 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 5.11 (dd, J = 12.5, 4.4 Hz, 1H), 4.83 (dd, J = 13.5, 4.5 Hz, 1H), 3.96–3.88 (m, 1H), 3.75 (s, 3H), 3.65 (q, J = 12.6 Hz, 1H), 3.48–3.40 (m, 1H), 2.78 (dt, J = 11.8, 4.5 Hz, 1H), 1.39 (d, J = 5.9 Hz, 3H), 1.37 (d, J = 6.5 Hz, 3H), 1.16 (d, J = 6.6 Hz, 3H), 1.02 (d, J = 6.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CS_2/$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated): δ = 158.65 (aryl *C*), 157.08, 156.78, 154.95, 154.48, 147.73, 147.35, 146.92, 146.74, 146.18, 146.08, 145.95, 145.93, 145.85 (2C), 145.75, 145.70, 145.62, 145.56, 145.49, 145.36, 145.06, 144.93, 144.89 (2C), 144.82 (2C), 144.76, 144.68, 144.30, 144.20, 144.11, 144.03, 142.88, 142.73, 142.35, 142.34, 142.31, 142.22, 142.14, 142.02, 141.98, 141.87 (2C), 141.75, 141.68, 141.49 (3C), 141.34, 141.29, 139.60, 139.20, 139.11, 139.05, 135.70, 135.31, 134.38, 133.67, 130.04 (2C, aryl *C*), 129.56 (aryl *C*), 113.76 (2C, aryl *C*), 76.30 (sp^3-*C* of C_{60}), 74.75 (sp^3-*C* of C_{60}), 70.91 (N*C*HCH$_2$), 56.19 (*C*HAr), 54.75 (O*C*H$_3$), 48.39 (br, N*C*H(CH$_3$)$_2$), 44.59 (br, N*C*H(CH$_3$)$_2$), 35.33 (CH*C*H$_2$CH), 25.33 (br, NCH(*C*H$_3$)$_2$), 22.74 (br, NCH(*C*H$_3$)$_2$), 21.70 (br, NCH(*C*H$_3$)$_2$), 21.33 (br, NCH(*C*H$_3$)$_2$) ppm; FT-IR (KBr): $\tilde{\nu}$ = 2959, 2927, 2865, 1612, 1513, 1461, 1427, 1363, 1251, 1216, 1178, 1113, 1038, 1008, 826, 574, 527 cm^{-1}; UV/Vis (CHCl$_3$): λ_{max} = 257, 322, 430, 714 nm; MS(MALDI-TOF): m/z: 968 $[M+1]^+$.

Preparation of 2a from C$_{60}$, Et$_3$N and *N*-methylglycine: The compound was prepared as described for **2a**, from C_{60}, **1a** and Et$_3$N: a mixture of C_{60} (36.0 mg, 0.05 mmol), *N*-methylglycine (4.5 mg, 0.05 mmol) and Et$_3$N (70 μL, 0.50 mmol) afforded unreacted C_{60} (16.6 mg, 46%) and adduct **2a** (15.8 mg, 40%).

Preparation of 2a from C$_{60}$, acetaldehyde and *N*-methylglycine: The compound was prepared as described for **2a**, from C_{60}, **1a** and Et$_3$N: the reaction of C_{60} (36.0 mg, 0.05 mmol) with *N*-methylglycine (4.5 mg, 0.05 mmol) and acetaldehyde (40% aqueous solution, 22 μL, 0.20 mmol) for 15 min gave unreacted C_{60} (14.0 mg, 39%) and adduct **2a** (20.2 mg, 51%). When the reaction was conducted at 110°C for 4 h, the same workup gave unreacted C_{60} (17.3 mg, 48%) and adduct **2a** (17.5 mg, 44%).

2′-Deutero-2′-trideuteromethyl-1′-methylpyrrolidino[3′,4′:1,9](C$_{60}$-*I*$_h$)-[5,6]fullerene (9): This compound was prepared as described for **2a**, from C_{60} (72.0 mg, 0.10 mmol), **1a** (7.7 mg, 0.05 mmol) and [D$_{15}$]triethylamine (139 μL, 1.00 mmol). Yield = 25.1 mg, 32%. Recovered C_{60}: yield = 34.9 mg, 48%. ^{1}H NMR (300 MHz, CS_2/C_6D_6): δ = 4.69 (d, J_{ab} = 9.3 Hz, 1H), 4.01 (d, J_{ab} = 9.3 Hz, 1H), 2.82 (s, 3H) ppm; ^{13}C NMR (75 MHz, CS_2/C_6D_6 with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated): δ = 156.50, 154.32, 154.09, 153.30, 147.42 (2C), 146.89, 146.81, 146.68, 146.51, 146.46, 146.35, 146.34, 146.27, 146.25, 146.14 (2C), 145.96, 145.71 (3C), 145.67, 145.58, 145.50, 145.44 (2C), 145.41, 145.36, 144.95, 144.83, 144.57, 144.56, 143.35, 143.34, 142.88, 142.85, 142.82, 142.80, 142.44, 142.39, 142.37, 142.35, 142.33, 142.25 (2C), 142.23 (2C), 142.13, 141.90, 141.87, 140.46, 140.41, 140.39, 140.00, 137.72, 136.68, 136.16, 135.93, 76.05 (sp^3-*C* of C_{60}), 70.37 (*C*H$_2$), 69.40 (sp^3-*C* of C_{60}), 39.59 (N*C*H$_3$) ppm; FT-IR (KBr): $\tilde{\nu}$ = 2943, 2770, 1637, 1510, 1460, 1425, 1330, 1185, 1156, 766, 574, 526 cm^{-1}; UV/Vis (CHCl$_3$): λ_{max} = 258, 322, 430, 704 nm; MS(MALDI-TOF): m/z: 795 $[M]^-$.

***cis*-4′-Deutero-3′-deuteromethyl-5′-(*N*,*N*-diethylamino)cyclopenta[1′,2′:1,9](C$_{60}$-*I*$_h$)[5,6]fullerene (14) and *cis*-4′-deutero-3′-(*N*,*N*-diethylamino)-5′-(4-methoxyphenyl)cyclopenta[1′,2′:1,9]-(C$_{60}$-*I*$_h$)[5,6]fullerene (15)**: This compound was prepared as described for **3**, from C_{60} (36.0 mg, 0.05 mmol), dried Et$_3$N (697 μL, 5.00 mmol), dried **4a** (304 μL, 2.50 mmol) and D$_2$O (40 μL, 2.00 mmol). Compound **14**: yield = 9.7 mg, 23%. Compound **15**: yield = 4.9 mg, 10%. Recovered C_{60}: yield = 7.2 mg, 20%. Compound **14**: ^{1}H NMR (400 MHz, CS_2/$CDCl_3$): δ = 4.87 (m, 1H), 3.69 (m, 1H), 3.18–3.08 (m, 2H), 3.03–2.93 (m, 2H), 2.89–2.80 (m, 0.37H), 2.75–2.67 (m, 0.28H), 1.88–1.84 (m, 0.57H), 1.17–1.10 (m, 6H) ppm. Compound **15**: ^{1}H NMR (400 MHz, CS_2/$CDCl_3$): δ = 7.52 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 5.05–4.99 (m, 1H), 4.85–4.80 (m, 1H), 3.60–3.54 (m, 0.34H), 3.76 (s, 3H), 3.30–3.17 (m, 2H), 3.15–3.00 (m, 2H), 2.89–2.82 (m, 0.27H), 1.21–1.14 (m, 6H) ppm.

***cis*-4′-Deutero-3′-(*N*,*N*-bis(pentadeuteroethylamino)-5′-(4-methoxyphenyl)cyclopenta[1′,2′:1,9](C$_{60}$-*I*$_h$)[5,6]fullerene (16)**: This compound was prepared as described for **3**, from C_{60} (36.0 mg, 0.05 mmol), **4a** (304 μL, 2.50 mmol) and [D$_{15}$]triethylamine (697 μL, 5.00 mmol). Yield = 18.2 mg, 39%. Recovered C_{60}: yield = 15.0 mg, 42%. ^{1}H NMR (300 MHz, CS_2/$CDCl_3$): δ = 7.51 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 4.84–4.78 (m, 1H), 3.75 (s, 3H), 3.60–3.51 (m, 0.72H), 2.86–2.81 (m, 0.62H) ppm.

Synthesis of 3 from C$_{60}$, diethylamine and acetaldehyde: The compound was prepared as described in the first preparation of **3**, but from C_{60} (36.0 mg, 0.05 mmol), diethylamine (104 μL, 1.00 mmol) and acetaldehyde (40% aqueous solution, 220 μL, 2.00 mmol) in ODCB (10 mL) for 30 min. Yield = 9.7 mg, 23%. Recovered C_{60}: yield = 8.8 mg, 24%.

Synthesis of 3 and 5a from C$_{60}$, diethylamine, acetaldehyde, and aldehyde 4a: The compounds were prepared as described for **3**, from C_{60} (36.0 mg, 0.05 mmol), diethylamine (259 μL, 2.50 mmol), acetaldehyde (40% aqueous solution, 275 μL, 2.50 mmol) and **4a** (304 μL, 2.50 mmol) for 30 min. Compound **3**: yield = 5.2 mg, 12%. Compound **5a**: yield = 4.9 mg, 10%. Recovered C_{60}: yield = 5.8 mg, 16%.

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