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A rigid macrocyclic bis-malonate for the regioselective preparation of trans-1 and trans-3 fullerene bis-adducts

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The polyfunctionalization of C₆₀ through multiple addition reactions has generated unprecedented stereochemical problems.¹ In the case of fullerene bis-adducts, mixtures of regioisomers are obtained by successive reactions at the C₆₀ core. Actually, mono-functionalized C₆₀ derivatives possess nine different 6–6 bonds (bonds at the junction between two six-membered rings) that can react in a second addition (Fig. 1).^{2,3} As a typical example, the sequential double Bingel cyclopropanation⁴ of C_{60} with 2-bromomalonate in the presence of a base gave seven out of the eight possible $C_{60}(C(CO_2Et)_2)_2$ bis-adducts,² only the *cis*-1 isomer was not formed for steric reasons. The first efficient methodology allowing the regioselective preparation of C₆₀ bis-adducts has been introduced by Diederich and co-workers.⁵ Starting from a mono-functionalized fullerene derivative in which the addend is carrying a reactive group at the end of a tether, they have shown that an intramolecular reaction provides a specific bis-adduct. The regioselectivity of the cyclization reaction results from the length of the spacer and steric constraints allowing the reactive group to attack a specific double bond on the fullerene scaffold. In a simplified version, C_{60} has been directly treated with a bis-functional reagent in which the two reactive groups are interconnected by a spacer.^{6,7} Macrocyclization reactions onto the C₆₀ core provide directly bis-adducts with good regioselectivities. This is for example the case for the reaction of C₆₀ with bis-malonates when quite rigid spacers are used.⁶ An alternative concept using flexible *cyclo*-oligomalonates has been also reported.⁸ The regioselectivity of these reactions is governed by the distribution of strain within the macrocycle and

the specific addition pattern of the product depends on the length of the spacers. In this Letter, we now show that this concept is not limited to flexible cyclobis-malonates. The reaction of C₆₀ with a rigid macrocyclic bis-malonate is also well suited for the regioselective preparation of specific fullerene bis-adducts.

The preparation of the rigid macrocyclic bis-malonate is depicted in Scheme 1. Treatment of alkyne $\mathbf{1}^9$ with *n*BuLi (1 equiv) in THF at 0 °C followed by reaction with di-tert-butylsilyl bis(trifluoromethanesulfonate) (tBu₂Si(OTf)₂, 0.5 equiv) gave 2 in 81% yield. Cleavage of the tetrahydropyran-2-yl (THP) protecting groups was then achieved by treatment of **2** with *p*-toluenesulfonic acid (pTsOH) in ethanol. Reaction of the resulting diol (3) with malonyl chloride in the presence of 4-dimethylaminopyridine (DMAP) under pseudo high dilution conditions afforded 4 in 9% yield.¹⁰ Macrocycle 4, which has a ring size of 40 atoms, was characterized by NMR spectroscopy and mass spectrometry. Crystals suitable for X-ray crystal analysis were also obtained by slow diffusion of npentane into a CH_2Cl_2 solution of **4**.¹¹ As shown in Figure 2, the X-ray crystal structural analysis of 4 reveals a centro-symmetrical structure for the macrocyclic bis-malonate with Si(1)-Si(1') and C(11)–C(11') distances of 10.424(1) and 17.688(2) Å, respectively.

The reaction of $\mathbf{4}$ with C_{60} was initially performed under the typical conditions developed by Diederich and co-workers for the preparation of fullerene bis-adducts from bis-malonates.^{6a} Specifically, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added to a solution of 4, C₆₀, and iodine in toluene at room temperature. Whereas reagent 4 was rapidly consumed, all the starting C_{60} was recovered at the end of the reaction thus showing that a fast decomposition of 4 occurred under these conditions. In order to prevent decomposition of this reagent, the reaction was then





ABSTRACT

A macrocyclic bis-malonate incorporating two rigid di(phenylethynyl)silane moieties has been prepared and used to functionalize C_{60} in a double Bingel cyclopropanation. Two regioisomeric bis-adducts have been thus obtained, namely the trans-1 and trans-3 isomers. The formation of these specific isomers is favored by both the size of the starting macrocycle and the minimum of strain in the final products. © 2013 Elsevier Ltd. All rights reserved.

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Figure 1. Addition of a second addend to a C_{2v} -symmetrical C_{60} mono-adduct can in principle lead to nine different regioisomeric bis-adducts. Relative to the first addend, the second one can be located either in the same hemisphere (*cis*), in the opposite hemisphere (*trans*), or on the equatorial belt (*e*). For identical addends, a second attack onto the *e*-edge or *e*-face positions leads to identical products. In the particular case of $C_{60}(C(CO_2Et)_2)_2$, the symmetry of the bis-adducts can be either C_2 (*cis*-3, *trans*-2, *trans*-3), C_s (*cis*-1, *cis*-2, *e*, *trans*-4), or D_{2h} (*trans*-1).



Scheme 1. Reagents and conditions: (i) *n*BuLi, THF, 0 °C, 1 h, then *t*Bu₂Si(OTf)₂, 0 °C, 1 h (81%); (ii) *p*TsOH, EtOH, rt, 12 h (78%); malonyl chloride, DMAP, CH₂Cl₂, rt, 12 h (9%); (iv) C₆₀, DBU, *I*₂, PhMe, -15 °C, 1 h (5: 8%, 6: 18%).

performed at lower temperatures. No reaction was observed at temperature lower than ca. -20 °C and the best results were obtained when the reaction mixture was stirred for 1 h at -15 °C. Under optimized conditions,¹² the reaction of **4** with C₆₀ gave the regioisomeric bis-adducts **5** and **6** in 8% and 18% isolated yields, respectively. Fullerene derivatives **5** and **6** were characterized by

¹H and ¹³C NMR, UV–vis, and IR spectroscopies. In addition, their structure was confirmed by MALDI-TOF mass spectrometry showing the expected molecular ion peak in both cases.¹²

In the case of **5**, the relative position of the two cyclopropane rings on the fullerene surface was unambiguously established by the D_{2h} symmetry deduced from the ¹H and ¹³C NMR spectra.



Figure 2. ORTEP plot of the structure of **4** (the thermal ellipsoids are shown at 50% probability level; C: gray; O: red, Si: yellow; H: white).

Among all the possible regioisomeric fullerene bis-adducts, a symmetry as high as D_{2h} can only be present if the addition pattern on the fullerene moiety is *trans*-1.¹³ Additionally, the greenish color and the absorption spectrum of **5** are also diagnostic signatures of a *trans*-1 addition pattern (Fig. 3).

The *trans*-1 addition pattern was nicely confirmed by the X-ray crystal structure analysis of **5**.¹⁴ As shown in Figure 4, compound **5** adopts a [1]rotaxane structure with the *trans*-1 C_{60} bis-adduct core located within the cavity of the surrounding macrocyclic bis-malonate. As observed for **4**, the structure of **5** is also centro-symmetric. However, due to the connection to the fullerene core, the Si(1)–Si(1') (16.280(2) Å) and C(31)–C(31') (9.923(6) Å) distances are significantly different for **5** when compared to **4**. Indeed, the two rigid bis(phenylethynyl)silane moieties are connected by two flexible malonate subunits providing sufficient adaptability to the system to form the *trans*-1 C_{60} bis-adduct during the double Bingel cyclopropanation.

The molecular symmetry (C_2) deduced from the ¹H and ¹³C NMR spectra of **6** suggests that this bis-adduct could be either a *trans*-2 or a *trans*-3 regioisomer. The UV–vis spectrum of **6** is indeed fully consistent with a *trans*-3 bis-adduct (Fig. 3). The absorption spectra of C_{60} bis-adducts being highly dependent on the addition pattern and characteristic for each of the regioisomers,^{2,6} the stereochemistry of compound **6** was thus elucidated. To further support this structural assignment, computational studies were also performed. The molecular geometry of the various regioisomers (*trans*-1, *trans*-2, and *trans*-3) was optimized with *spartan'10* Macintosh Parallel Edition (Wavefunction Inc., USA) at the AM1



Figure 3. Absorption spectra (CH_2Cl_2) of compounds **5** and **6** revealing the characteristic features of *trans*-1 (**5**) and *trans*-3 (**6**) bis-addition patterns.



Figure 4. ORTEP plots of the structure of **5** (the thermal ellipsoids are shown at 50% probability level; C: gray; O: red, Si: yellow; H: white; the co-crystallized CHCl₃ molecules are not shown for clarity).

semi-empirical level. The *trans*-2 isomer was effectively found noticeably higher in energy than **5** ($\Delta E = -22$ kJ/mol) and **6** ($\Delta E = -41$ kJ/mol). Importantly, the increase in energy observed when going from the *trans*-3 (**6**) to the *trans*-1 isomer (**5**) is in good agreement with the experimental product distribution. The difference in heat of formation for the various regioisomers reflects the difference in strain within the rigid parts of the macrocyclic bismalonate. The two regioisomers in which this strain is minimal are actually formed in the double Bingel cyclopropanation of C₆₀ with bis-malonate **4**. In contrast, the steric constraints are too important in the case of the *trans*-2 regioisomer thus its formation is prevented.

In conclusion, the reaction of a rigid macrocyclic bis-malonate with C_{60} gave access to fullerene bis-adducts with an excellent regioselectivity. The formation of specific isomers is favored by both the size of the starting macrocycle and the minimum of strain in the final products. With its *trans*-1 addition pattern combined to a peculiar [1]rotaxane structure, bis-adduct **5** is perfectly suited for further functionalization with two additional malonate moieties to produce fullerene tetra-adducts with a D_{2h} -symmetrical all-*e* addition pattern.^{15,16} In this way, a wide range of unprecedented nanomaterials constructed around a central fullerene core will become accessible. This will be easily achieved by combining this chemistry with our approach based on the use of click reactions for the successive grafting of different functional groups onto the fullerene scaffold.¹⁷ Work in this direction is under way in our laboratory.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/i.tetlet.2013. 04.024.

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- 11. Crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of n-pentane into a CH₂Cl₂ solution of 4. Data were collected at 173 K on a Bruker APEX-II CCD diffractometer (MoK α radiation, λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-97) and refined against F^2 using the shelxl-97 software. The nonhydrogen atoms were refined anisotropically, using weighted full-matrix least-squares on F^2 . The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters.

Crystallographic data: formula: $C_{58}H_{64}O_8Si_2$ ($M = 945.27 \text{ g mol}^{-1}$); crystal system: monoclinic, space group P 21/c; a = 8.0891(4) Å; b = 11.9245(6) Å; c = 28.5114(14) Å; $\beta = 97.852(1)^\circ$; V = 2724.4(2) Å³; Z = 2; F(000) = 1008; a total of 23,609 reflections collected; $1.85^{\circ} < \theta < 30.00^{\circ}$, 7933 independent reflections with 4572 having $I > 2\sigma(I)$; 313 parameters; final results: $R_1(F^2) = 0.0524$; $wR_2(F^2) = 0.0985$, goof = 1.002 (CCDC 927709)

- 12. Compounds 5 and 6. DBU (0.16 mL, 1.06 mmol) was added to a stirred solution of C_{60} (156 mg, 0.22 mmol), I_2 (138 mg, 0.54 mmol), and ${\bf 4}$ (205 mg, 0.22 mmol) in a mixture of toluene (312 mL) and CH_2Cl_2 (30 mL) at -15 °C. The resulting solution was stirred for 1 h, then filtered through a short plug of SiO2 (CH2Cl2) and evaporated. Column chromatography (SiO2, toluene/ cyclohexane 6:4) gave 5 (30 mg, 8%) and 6 (66 mg, 18%). Compound 5: Greenish-brown solid. IR (neat): 2160 (C=C), 1732 (C=O). UV/vis (CH₂Cl₂): 246 (100,500), 256 (105,900), 327 (24,000), 410 (sh, 2800), 442 (1900), 471 (2500). ¹H NMR (400 MHz, CDCl₃): 7.47 (d, J = 8 Hz, 8H), 7.36 (d, J = 7 Hz, 8H), 5.58 (s, 8H), 1.13 (s, 36). ¹³C NMR (100 MHz, CDCl₃): 163.7, 144.7, 144.2, 144.1, 143.3, 142.2, 140.9, 138.2, 134.9, 132.5, 131.3, 125.0, 106.0, 90.3, 69.7, 69.3, 43.6, 28.1, 27.9, 20.0. MS (MALDI-TOF): 1661 ([M]⁺, calcd for C₁₁₈H₆₀O₈Si₂: 1661.9). Compound 6: Dark brown solid. IR (neat): 2160 (C=C), 1727 (C=O). UV/vis (CH2Cl2): 252 (155,700), 272 (sh, 97400), 320 (sh, 30,400), 380 (7900), 411 (3400), 422 (2700), 488 (2400), 580 (sh, 800), 638 (sh, 300), 688 (200). ¹H MR (400 MHz, CDCl₃): 7.44 (d, *J* = 7 Hz, 4H), 7.37 (d, *J* = 7 Hz, 4H), 7.33 (d, *J* = 7 Hz, 4H), 7.37 (d, *J* = 11 Hz, 2H), 5.57 (d, *J* = 11 Hz, 2H), 5.34 (d, J = 11 Hz, 2H), 5.15 (d, J = 11 Hz, 2H), 1.12 (s, 18H), 1.11 (s, 18H). ¹³C NMR (100 MHz, CDCl₃): 163.0, 162.7, 146.6, 146.4 (two peaks), 146.2, 145.8, 145.7, 145.5, 145.2, 145.0, 144.6, 144.4, 144.3, 144.2, 144.1, 143.6, 143.2 (two peaks), 143.1, 143.0, 142.3, 142.0, 141.7, 141.4, 141.1, 139.9, 138.3, 136.8, 134.9, 134.7, 132.4, 132.0, 130.8, 130.6, 124.7, 124.5, 106.4 (two peaks), 90.7, 90.4, 71.3, 70.9, 69.2, 69.1, 51.9, 28.0, 27.9, 19.3. MS (MALDI-TOF): 1660.4 ([M]⁺, calcd for C₁₁₈H₅₉O₈Si₂: 1660.9).
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- 14. Crystals suitable for X-ray crystal structure analysis were obtained by slow evaporation of a CS₂/CHCl₃ solution of 5. Data were collected at 173 K on a Bruker APEX-II CCD diffractometer (MoK α radiation, $\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELXS-97) and refined against F^2 using the SHELXL-97 software. The nonhydrogen atoms were refined anisotropically, using weighted full-matrix least-squares on F^2 . The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. Crystallographic data: formula: $(C_{118}H_{60}O_8Si_2)(CHCl_3)_2$ (M = 1900.58 gmol⁻ crystal system: monoclinic, space group P 21/c; a = 13.7434(10) Å; b = 24.2628(17) Å; c = 12.8120(9) Å; $\beta = 95.214(2)^{\circ}$; V = 4254.5(5) Å³; Z = 2; F(000) = 1952; a total of 30,649 reflections collected; $1.68^{\circ} < \theta < 28.27^{\circ}$, 10,442 independent reflections with 5488 having $I > 2\sigma(I)$; 619 parameters; final results: $R_1(F^2) = 0.0879$; $wR_2(F^2) = 0.2374$, goof = 1.052 (CCDC 927710).
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