[5,6]-Open Methanofullerene Derivatives of $I_h$-$C_{80}$**

Marta Izquierdo, Maira R. Cerón, Marilyn M. Olmstead, Alan L. Balch,* and Luis Echegoyen*

The synthesis of novel endohedral metallofullerene (EMF) derivatives has attracted considerable attention, mainly because of their exceptional electronic properties.[1–3] The exploration of new derivatization protocols to increase their solubility and processability is crucial to expand the range of potential applications of these compounds.[4–6] In general, EMFs show low reactivity owing to the pronounced stabilization that results from extensive charge transfer between the encapsulated metal cluster and the carbon cage.[7] It is well-known that cycloaddition reactions of azomethine ylides[8] Diels–Alder reactions,[9] and [2+2] cycloaddition reactions,[10] proceed well with triselctalic nitride endohedrals only if a large excess of the reagents and long reaction times are used. An interesting observation concerning the most studied EMF, Sc$_3$N@$I_h$-$C_{60}$, is its lack of reactivity under regular Bingel–Hirsch conditions.[11] Sc$_3$N@$I_h$-$C_{60}$ reacts only in the presence of dimethyl formamide.[12]

Cyclopropanation-type reactions have been used to modify EMFs to yield methanofullerenes[13] and recently, azafulleroids[14] and silylene-bridged derivatives.[15] There are two distinct addition sites available on the $I_h$ isomer of $C_{60}$ fullerenes: C–C bonds at [6,6] ring junctions (pyrene-type sites) and C–C bonds at [5,6] ring junctions (corannulene-type sites). In 2005, Poblet and co-workers[16] reported that the corannulene [5,6] bonds closest to the Sc atoms have the highest strain of all bonds in the $I_h$-$C_{60}$ cage. Reactions at this bond can relieve some of the strain and produce the thermodynamically more stable derivative; therefore, the [5,6] bond is more reactive toward endohedral functionalization. This hypothesis was experimentally corroborated for reactions such as Diels–Alder[17] and 1,3-dipolar cycloaddition reactions.[8,18] However, the [6,6] junction is favored for methano-bridge formation on $I_h$-$C_{60}$.[13,19,20] Although nitrogen[14] and silicon bridges[15] at [5,6] bonds have been reported, the corresponding methano adducts have remained elusive.

Phenyl-C$_7$-butyric acid methyl ester (PC$_7$BM) and phenyl-C$_7$-butyric acid methyl ester (PC$_7$BM) are well-known electron acceptors that exhibit reasonable efficiencies in organic photovoltaic (OPV) devices.[21] In general, solubility and processability is crucial to expand the range of potential applications of these compounds. [4–6] In general, EMFs show low reactivity owing to the pronounced stabilization that results from extensive charge transfer between the encapsulated metal cluster and the carbon cage.[7] It is well-known that cycloaddition reactions of azomethine ylides[8] Diels–Alder reactions,[9] and [2+2] cycloaddition reactions,[10] proceed well with triselctalic nitride endohedrals only if a large excess of the reagents and long reaction times are used. An interesting observation concerning the most studied EMF, Sc$_3$N@$I_h$-$C_{60}$, is its lack of reactivity under regular Bingel–Hirsch conditions.[11] Sc$_3$N@$I_h$-$C_{60}$ reacts only in the presence of dimethyl formamide.[12]

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confirmed the presence of the molecular-ion peak for the monoadduct products (m/z 1430.7875 for (p-Br)DPM-Sc-N@I-C80; m/z 1274.0074 for DPM-Sc-N@I-C80 [M–H]–; and m/z 1475.0458 for (p-C6H13O)2DPM-Sc-N@I-C80; see Figures 4S, 7S, and 16S, respectively, in the Supporting Information).

The 1H NMR spectra in most cases clearly showed the presence of two products with different symmetry. Purification of the mixture by preparative recycling HPLC (with a Buckyclutcher column; Figure 1) enabled the isolation of 2 and 3 in different ratios, depending on the para substitutent on the aromatic ring (2a/3a 1:6; 2b/3b 1:5; 2c/3c 1:3).

The 1H NMR spectroscopic signals for the aryl hydrogen atoms of 2c appear as four doublets (δ = 6.82, 6.95, 7.65, and 8.16 ppm; see Figure 12S). Thus, 2c is the [5,6] addition product, and 3c is the [6,6] product (Figures 2 and 3c). Compounds 2a–c and 3a,b exhibited similar spectra (see the Supporting Information). 13C NMR and UV/Vis spectroscopy were used to establish whether the addition reactions resulted in open- or closed-cage structures. The 13C NMR spectroscopic experiment was only possible for 3e because it was obtained in reasonable amounts. The 13C NMR spectrum of compound 3e exhibited 40 signals for sp2 carbon atoms and two signals for the equivalent sp2 carbon atoms of the phenyl rings (δ = 128.47 and 114.72 ppm; see Figure 13S), in agreement with the expected symmetry of the [6,6] product. The chemical shift of the methano-bridge carbon atom (δ = 67.90 ppm) is similar to those of other reported open cyclopropanyl derivatives.[25] The UV/Vis absorption spectra of 2c and 3e showed similar patterns to those of pristine Sc3N@I-C80. The similarity of the spectra suggests that the electronic structure of the C80 cage is minimally perturbed and indicates that both compounds probably have open structures (fulleroids; see Figure 17S).

The diaryl carbene 1e is remarkably reactive, as evidenced by the formation of 2c and 3e (1:3 ratio; Figure 3c) in chlorobenzene at −40°C. The mixture of monoadducts was obtained in 40% yield, which is only slightly lower than that observed when the reaction was carried out at 0°C (48%).

As already mentioned, typical cyclopropanation reactions of Sc3N@I-C80 require a large (sometimes 100-fold)[24] excess of the carbene reagent and afford the [6,6] adducts exclusively. In the present study, when the reaction was conducted in o-DCB (100°C, in the dark, 2 h; route B) only one equivalent of 1 was required for the formation of the products in reasonable yield. The products were obtained in similar ratios to those found for the photochemical reaction, with the exception of 2a and 3a, in which case the ratio increased from 1:8 to 1:6 (Figure 3a,b). The substituent group at the para position of the aryl group clearly influences the reactivity of the carbene and therefore affects the yield of 2. When the substituent was electron-withdrawing (R = Br), less of product 2 was formed than with an electron-donating substituent (R = OCH3H13). The new [5,6]-modified compounds exhibited very high stability, even upon heating for long periods (reflux in o-DCB, 16 h) or irradiation (λ = 350 nm, o-DCB, 6 h). No evidence of isomerization was observed.

Single crystals of 3e were grown from a solution in CS2/hexanes by slow diffusion. The asymmetric unit contained one molecule of the open [6,6]-DPM adduct of Sc3N@I-C80 and 0.5 molecules of CS2 (see Figure 18S). The Sc3N group is positioned such that one Sc (Sc1) atom is nestled close to the extra interior space created by adduct formation (the distance from the centroid of C1–C9 to Sc1 is 2.220 Å). If the minor Sc4 disorder is neglected, the tr-metallic nitride group is planar, with the sum of the Sc-N-Sc angles equal to 359.8°. The atoms at the open [6,6] junction, C1 and C9, are highly pyramidalized, and the addition of the central methano carbon atom (C81) results in a stretch from...
a typical [6,6] distance of 1.42 Å to a distance of 2.12(3) Å between C1 and C9 (see Figure 18Sb). In the crystal structure, a second molecule, generated by the glide, is embraced by the phenyl “arms” of the first molecule through π–π and van der Waals interactions (see Figure 19S).

Single crystals of 2c were grown from a solution in CS2/CDCl3/hexanes by slow diffusion. The asymmetric unit contained one molecule of the open [5,6]- (p-C6H13O)2DPM adduct of Sc3N@Ih-C80 (Figure 4a). Data collection and structure solution were conducted as for [6,6]- (p-C6H13O)2DPM-Sc3N@Ih-C80·0.5(CS2) (3c; see the Supporting Information). The poor agreement factors for this structure are probably the result of several factors: the small crystal size, loss of the solvent CS2 or disorder of CS2, 50:50 disorder in the fullerene orientation, and disorder in the alkyl chains. Surprisingly, the structure itself is clear, and we feel that the result is valid. The questions to be answered were 1) whether or not the modification had occurred at a [5,6] junction, at which a pentagon and a hexagon are joined, and 2) whether the [5,6] bond was open or closed. The location of the modification at a [5,6] junction was apparent from an early stage of the crystal-structure solution, and the methano bridge spans a distance of 2.23(4) Å; thus, the structure is “open”. The structure resembles that of the [6,6] isomer in general. The Sc3N unit is planar, and one of the three Sc atoms is close to the opening in the cage. The distance from the centroid of C1–C2 to Sc1 is 2.223 Å. The DPM “arms” embrace a neighboring C80 cage in a similar manner to that exhibited by the [6,6] isomer 3c. A distinct void space is present in which a solvent CS2 molecule would be expected but was not located. As was true for the [6,6] isomer, there are two rotational orientations for the C80 cage, and their occupancy is close to 50:50 in the case of the [5,6] isomer.

The redox potentials of 2c and 3c were measured by cyclic voltammetry (CV) and square wave voltammetry (SWV) in o-dichlorobenzene. The SWV results are summarized in Table 1. Previous studies showed that [5,6] adducts resulting from 1,3-dipolar cycloaddition reactions typically exhibit reversible cathodic electrochemical behavior, whereas [6,6] adducts typically exhibit irreversible behavior.
Table 1: Redox potentials of 2c, 3c, and Sc3N@Ic-C80.

<table>
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<tr>
<th>Compound</th>
<th>E&lt;sup&gt;-1/2&lt;/sup&gt;</th>
<th>E&lt;sup&gt;0+&lt;/sup&gt;</th>
<th>E&lt;sup&gt;-1/2&lt;/sup&gt;</th>
<th>E&lt;sup&gt;-3/2&lt;/sup&gt;</th>
<th>E&lt;sup&gt;-3/4&lt;/sup&gt;</th>
<th>E&lt;sup&gt;-5/6&lt;/sup&gt;</th>
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<tr>
<td>2c</td>
<td>–</td>
<td>–</td>
<td>–1.19</td>
<td>–1.51</td>
<td>–1.92</td>
<td>–2.25</td>
</tr>
<tr>
<td>3c</td>
<td>–</td>
<td>+0.52</td>
<td>–1.51</td>
<td>–1.61</td>
<td>–2.23</td>
<td>–2.35</td>
</tr>
<tr>
<td>Sc3N@Ic-C80</td>
<td>+1.09</td>
<td>+0.59</td>
<td>–1.26</td>
<td>–1.62</td>
<td>–2.37</td>
<td>–</td>
</tr>
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</table>

[a] Values obtained by SWV in volts versusFc/Fc’. [b] Data from Ref. [16].

Experimental Section

The synthesis and purification of Sc3N@Ic-C80,[24] the experimental details, and the characterization of the products are included in the Supporting Information, as well a diagram showing the numbering scheme for Ic-C80 (see Figures 18S and 19S) and X-ray crystallographic files for [5,6]-[p-OCH3]2DPM-Sc3N@Ic-C80.0.5CS2 and [5,6]-[p-OCH3]2DPM-Sc3N@Ic-C80.0.5CS2[24] were selected for data collection on a Bruker D8 diffractometer equipped with an ApexII CCD detector at the Advanced Light Source, Berkeley, CA, beamline 11.3.1. Data was collected at 90(2) K by the use of Bruker SAINT software package[27] and a multiscan absorption correction was applied by the use of the program SADABS.[28] The structures were solved by using the SHELXT software package[29] and refined by full-matrix least-squares on F<sup>2</sup> (SHELXL-2013).[30] There are two orientations for the C80 cage in both structures, and these orientations were modeled by the use of rigid groups corresponding to well-determined structures of Ic-C80, whereas the refinement of carbon atoms in the region of the modification was allowed to proceed. Relative occupancies for the two orientations were 0.500.50 (fixed) for the [5,6]isomer and 0.691(4)/0.309(4) (refined) for the [6,6] isomer. The encaged Sc3N moiety was ordered in the case of the [5,6] isomer and suffered minor disorder with a Sc2/Sc4 set at a 0.895(6)/0.104/18 ratio in the [6,6] isomer. Crystal data for 2c: C105H34NO2Sc3, M<sub>r</sub> = 1476.21, monoclinic, P2<sub>1</sub>/c, a = 11.153(8), b = 32.36(2), c = 17.024(12) Å, β = 90.640(8)°, V = 5960(7) Å<sup>3</sup>, Z = 4, R1 [3740 reflections with I > 2σ(I)] = 0.092, wR2 (all 4678 data) = 0.633, 319 parameters, 30 restraints. Crystal data for 3c:

Figure 4. a) A view of the asymmetric unit of 2c. The disorder in the C80 orientation is omitted for clarity. Displacement parameters are shown at the 35 % probability level. b) A view from inside the Ic cage of 2c in the vicinity of the open [5,6] junction. The DPM adduct spans C1-C2 at a distance of 2.23(4) Å. Another orientation is present, but the two atoms C1 and C2 belong to both parts of the molecule. The expected [5,6] distance in Ic-C80 is approximately 1.45 Å.
Keywords: [5,6]-open isomers - diazo compounds - endohedral fullerenes - icosahedral C_{60} - methanofullerenes