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A Symmetric Derivative of the Trimetallic Nitride Endohedral Metallofullerene, $Sc_3N@C_{80}$

Erick B. Iezzi,[§] James C. Duchamp,[‡] Kim Harich,[§] Tom E. Glass,[§] Hon Man Lee,[†]
Marilyn M. Olmstead,[†] Alan L. Balch,[†] and Harry C. Dorn*,[§]

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

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Over the past decade, organic functionalization chemistry of the empty-cage C_{60} fullerene has grown exponentially since the molecule was discovered to possess reactive double bonds at the [6,6] ring junctures of the cage, otherwise known as pyracyclene-type units.[1−5] Each C_{60} molecular cage contains six of these reactive units; however, the [6,6] junctures of larger empty cages (i.e., C_{70} and C_{78}) are not necessarily as reactive as C_{60} due to cage shape and strain.[6,7] Although novel derivatives of empty cages have been synthesized, functionalized endohedral metallofullerenes hold a greater promise for creating unique molecules with extraordinary properties, due to the wide variety of metals and metal clusters that can be encapsulated inside the carbon cages.[8−12] Unfortunately, little is known of cage structure and reactivity for most endohedral metallofullerenes, which are produced in much smaller quantities than most empty-cage fullerenes.

Recently, high yields of novel trimetallic nitride endohedral metallofullerenes[13−15] have been produced by introducing nitrogen gas into the Krätschmer−Huffman generator during vaporization of packed graphite rods containing various metal oxides, known as the trimetallic nitride template (TNT) process. The most abundant trimetallic nitride, $Sc_3N@C_{80}$, can be formally viewed as a positively charged planar cluster of atoms inside a negatively charged icosahedral carbon cage, $[Sc_3N]^{+6}@[C_{80}]^{-6}$. Although both C_{60} and the C_{80} carbon cage of $Sc_3N@C_{80}$ exhibit icosahedral symmetry (I_h),[16,17] C_{60} consists of a single pyracyclene-type carbon whereas the $Sc_3N@C_{80}$ cage is composed of two types of carbon atoms: a pyrene-type carbon (intersection of three six-membered rings) and a corannulene-type carbon (intersection of a five-membered ring and two six-membered rings).[13] The C_{80} (I_h) cage does not possess pyracyclene-type reactive sites for functionalization to occur; therefore, other reactive sites must be present to functionalize the molecule.

Herein, we propose a structure for a symmetric derivative of the trimetallic nitride endohedral metallofullerene, $Sc_3N@C_{80}$, formed when reacted with ^{13}C labeled 6,7-dimethoxyisochroman-3-one (**1**).

A 1,2,4-trichlorobenzene solution containing $Sc_3N@C_{80}$ (6.5 mg, 99%) (**2**) was refluxed for 24 h with an excess of 6,7-dimethoxyisochroman-3-one (99% ^{13}C labeled) (**1**)[18] to achieve the novel ^{13}C labeled metallofullerene monoadduct **3** (Scheme 1).[19] The crude reaction solution was dominated by a single reaction product (Figure 1a) and was purified by HPLC methods using a Trident-Tri-DNP column (Buckyclutcher column: Regis Chemical) with chloroform as the eluent.

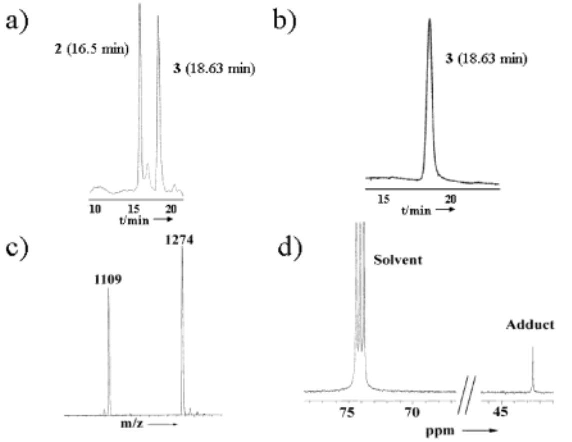
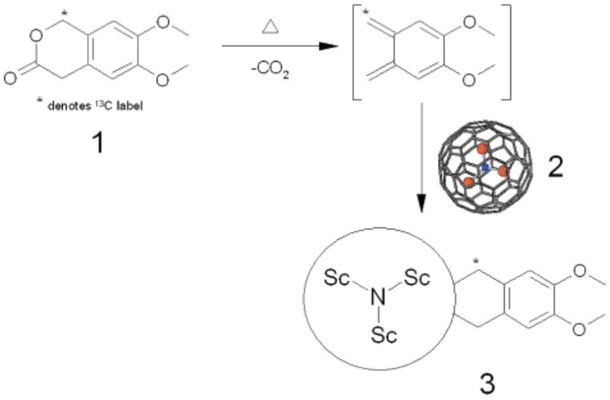


Figure 1. (a) HPLC chromatogram of monoadduct **3** and unreacted $Sc_3N@C_{80}$ (**2**) in crude reaction solution, (b) HPLC trace of purified monoadduct **3**, (c) MALDI-TOF mass spectrum of pure **3** (^{13}C labeled) using a 9-nitroanthracene matrix and negative ionization, and (d) ^{13}C NMR of monoadduct **3**.

Scheme 1



The matrix assisted (9-nitroanthracene[20]) laser desorption ionization time-of-flight mass spectrum (MALDI-TOF MS) of **3** (Figure 1c) displays a peak for the ^{13}C labeled monoadduct at m/z 1274 and a peak at m/z 1109 for the cleaved adduct. The newly synthesized adduct **3** yields a molecular ion peak at a higher abundance than the parent endohedral metallofullerene, which contrasts with previously reported mass spectra of functionalized endohedral metallofullerenes.[21] Adducts of higher mass were not observed within the spectrum.

The small quantity (<1 mg) of ^{13}C labeled adduct **3** exhibits a ^{13}C NMR with a single narrow signal at 42.25 ppm for the equivalent methylene carbons (Figure 1d).[22] This suggests the presence of plane symmetry for adduct **3**. The hydrogens attached

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[‡] Department of Chemistry, Emory and Henry College, P.O. Box 947, Emory, VA 24327.
[†] Department of Chemistry, University of California, Davis, CA 95616.
[§] Virginia Polytechnic Institute and State University, Blacksburg.

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Table 1. ^{1}H and ^{13}C NMR Peak Comparison (ppm) of the $Sc_3N@C_{80}$ and C_{60} Adducts

	$Sc_3N@C_{80}$ adduct (3)	C_{60} adduct[19]
methylene carbon	42.25	46.62
methylene protons	3.41 and 3.57	4.37 and 4.74
methoxy carbon	55.93	58.20
methoxy protons	3.98	4.01
sp^3 carbon on cage	52.30	67.94
phenyl protons	7.01	7.20

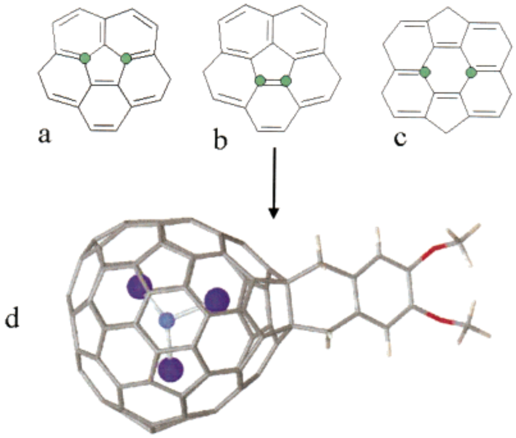

Figure 2. Motifs of possible reactive sites on the I_h $Sc_3N@C_{80}$ cage: (a) 1,3 position on a five-membered ring, (b) 1,2 position on a five-membered ring, (c) 1,4 position on a six-membered ring, and (d) Gauss View structure of the proposed adduct from addition of **1** to a double bond (site "b") on the cage.

to the methylene carbons of **3** are nonequivalent and centered at 3.41 and 3.57 ppm, respectively.[23] The $^1J_{CH}$ coupling within the methylene groups is ~133 Hz.

Implementation of HMQC (Heteronuclear Multiple Quantum Coherence)[24] verifies that the two sets of nonequivalent methylene hydrogens are attached to equivalent carbon atoms of a symmetric adduct, and also provides the ^{13}C NMR chemical shift of the methoxy carbons (55.93 ppm) on adduct **3**. The ^{13}C chemical shifts of adjacent carbon atoms to the methylene carbons were achieved by using HMBC (Heteronuclear Multiple Bond Coherence).[25] Hydrogens of the methylene groups are coupled, via 2-bond coupling ($^2J_{CH}$), to the sp^3-hybridized carbon atoms of the metallofullerene cage (52.30 ppm), which is the site where the reaction has occurred. In addition, the hydrogens are also coupled ($^2J_{CH}$) to the sp^2-hybridized carbons of the phenyl ring (126.53 ppm). The ^{13}C NMR structural data comparison of adduct **3** and the previously synthesized C_{60} adduct[19] are presented in Table 1.

The suggested symmetry plane of monoadduct **3** is plausible by reagent **1** addition to one of only three sites on the I_h $Sc_3N@C_{80}$ cage, as illustrated in Figure 2. The mechanistic pathway of reagent **1** addition has been shown to occur via a [4 + 2] cycloaddition,[19] thus reacting with a localized double bond at a [5,6] ring juncture (Figure 2b) on the cage. Additions to reactive sites "a" and "c" are less likely and would lead to highly strained adducts. A structure of the proposed site "b" addition adduct (Figure 2d) conserves a symmetry plane within the cage of the proposed structure. The position of the trimetallic nitride cluster inside the cage is shown only for illustrative purposes.

In summary, we have successfully synthesized and characterized the first organic derivative of a trimetallic nitride endohedral metallofullerene. The data indicates that monoadduct **3** dominates the reaction, and that the novel adduct possesses a plane of symmetry. A structure has been proposed that is consistent with the experimental data, although X-ray crystallographic[27] and 2D ^{13}C NMR studies are planned for further structure elucidation.

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Supporting Information Available: HMQC, HMBC, and COSY spectral data of monoadduct **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) ^{13}C NMR (90 MHz, $C_2Cl_4D_2$): δ 42.25 (s, CH_2).
(23) ^{1}H NMR (400 MHz, $C_2Cl_4D_2$): δ 3.41 (m, 2H, CH_2), 3.57 (m, 2H, CH_2), 3.98 (s, 6H, OCH_3), 7.01 (s, 2H, CH).
(24) HMQC (500 MHz, $C_2Cl_4D_2$): Supporting Information.
(25) HMBC (500 MHz, $C_2Cl_4D_2$): Supporting Information.
(26) COSY (500 MHz, $C_2Cl_4D_2$): Supporting Information.
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