Fullerene Chemistry

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The Cycloaddition Reaction of I_h-$Sc_3N@C_{80}$ with 2-Amino-4,5-diisopropoxybenzoic Acid and Isoamyl Nitrite to Produce an Open-Cage Metallofullerene**

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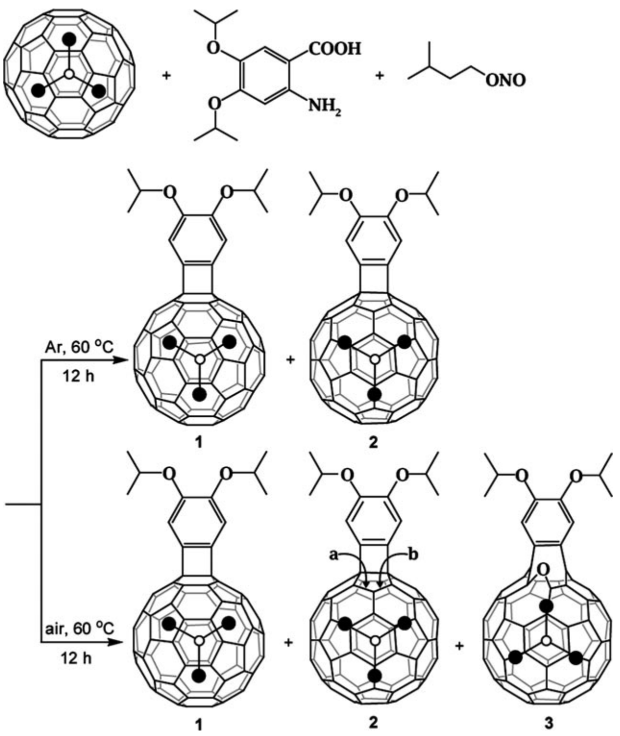
The unique structural and electronic properties of endohedral metallofullerenes (EMFs) make them candidates for applications in nanoscience and biomedicine, and the functionalization of EMFs has attracted increasing attention.[1] Various types of transformations, such as Diels–Alder reactions, 1,3-dipolar cycloadditions, photochemical silylation, alkylation and carbene additions, Bingel reactions, and free-radical reactions have been reported to take place on the outer surface of EMFs.[1] Icosahedral (I_h) $Sc_3N@C_{80}$, the most abundant EMF, can undergo most, but not all, of the above-mentioned reactions.[2] For example, the Bingel reaction of I_h-$Y_3N@C_{80}$[3a,c] and I_h-$Gd_3N@C_{80}$[3b] has been reported to yield methanofullerene derivatives, but the same attempted cyclopropanation reaction with I_h-$Sc_3N@C_{80}$ was not successful.[3a] The [2+2] cycloaddition of benzyne, which is known to occur with C_{60}[4a] and C_{70},[4b] has only recently been reported to occur with EMFs.[5] Herein, we report that the [2+2] cycloaddition of I_h-$Sc_3N@C_{80}$ with 4,5-diisopropoxybenzyne generated in situ from 2-amino-4,5-diisopropoxybenzoic acid and isoamyl nitrite in 1,2-dichlorobenzene (ODCB) in the presence of air produces an unprecedented open-cage metallofullerene.

The reaction of I_h-$Sc_3N@C_{80}$ with 2-amino-4,5-diisopropoxybenzoic acid and isoamyl nitrite in a molar ratio of 1:5:6 in ODCB at 60 °C for 12 h under argon atmosphere afforded an isomeric mixture of [2+2] cycloadducts **1** and **2** in 29% combined yield along with 48% of recovered I_h-$Sc_3N@C_{80}$ (Scheme 1). The ratio of cycloadducts **1** and **2** was 29:71 (8%:21%) based on the ^{1}H NMR spectrum of the mixture.



Scheme 1. Reaction of I_h-$Sc_3N@C_{80}$ with 2-amino-4,5-diisopropoxybenzoic acid and isoamyl nitrite under argon or air. Scandium atoms: ●; nitrogen atoms: ○.

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Adducts **1** and **2** could be separated by recycling high-performance liquid chromatography (HPLC) on a Buckyprep column with toluene as the mobile phase. Analogous products were recently reported from the reaction of I_h-$Sc_3N@C_{80}$ with 2-aminobenzoic acid and isoamyl nitrite.[5a]

Surprisingly, when the reaction was conducted in air under otherwise identical conditions, an unusual open-cage metallofullerene **3** was formed along with **1** and **2**. Further investigation showed that the yield of **3** was highly dependent on the amount of isoamyl nitrite and water present under these aerobic conditions. We found that **3** became the major product at the expense of **2** when the reaction of I_h-$Sc_3N@C_{80}$ with 2-amino-4,5-diisopropoxybenzoic acid and isoamyl nitrite (reactant ratio: 1:5:8) was conducted in the presence of 25 equiv of water under aerobic conditions at 60 °C for 12 h. Products **1**–**3** were formed in 22 % combined yield with 46 % of unreacted I_h-$Sc_3N@C_{80}$ recovered (see Scheme 1). The ratio of **1**/**2**/**3** was 32:14:53 (7 %:3 %:12 %) as calculated from the ^{1}H NMR spectrum of the mixture. The separation of products **1**–**3** was achieved by recycling HPLC. When more than 8 equiv of isoamyl nitrite were employed in the reaction, **2** could be completely converted to **3**, although the yield was lower because the excess isoamyl nitrite decomposed the products as well as the starting compound I_h-$Sc_3N@C_{80}$.

Products **1**–**3** were characterized by MALDI-TOF MS, ^{1}H NMR, and UV/Vis-NIR spectroscopy, and **3** was identified by single-crystal X-ray diffraction. The mass spectra of both **1** and **2** gave the same mass peak at m/z 1301, which is consistent with their identities as isomeric 4,5-diisopropoxybenzyne adducts of I_h-$Sc_3N@C_{80}$. In contrast, the MS of **3** showed a mass peak at m/z 1317. The mass number difference of 16 between **3** and **1** or **2** suggested that an additional oxygen atom was added to the benzyne adduct to form **3**. The ^{1}H NMR spectra of **1**–**3** are shown in Figure 1. In the ^{1}H NMR spectra of **1** and **2**, two groups of signals (two doublets with $J = 6.0$ Hz) for the four methyl groups were observed for both products, while two singlets and only one singlet were found for the two aromatic protons of adducts **1** and **2**, respectively. These ^{1}H NMR data indicated that both **1** and **2** had a mirror-plane symmetry element, which is in the plane of the phenyl ring for adduct **1**, whereas it is perpendicular to the plane of the phenyl ring for adduct **2**. For I_h-$Sc_3N@C_{80}$, only two types of C–C double bonds, that is, [5,6] and [6,6] ring junctions, are available for a cycloaddition reaction.[1] Therefore, products **1** and **2** can be assigned as the [6,6]-regioisomer and [5,6]-regioisomer, respectively.

The assignments of **1** and **2** were further confirmed by their UV/Vis-NIR spectra (Figure 2). Product **1** showed a broad absorption band centered at 800 nm, a characteristic peak for a [6,6]-regioisomer of I_h-$Sc_3N@C_{80}$,[2d] while **2** displayed absorptions at $\lambda = 333$, 372, 420, 468, 570, 710, 842, and 955 nm. These spectra are analogous to the spectra of the corresponding benzyne adducts and indicate that the presence of the alkoxy substituents does not alter the structure of the adducts.[5a]

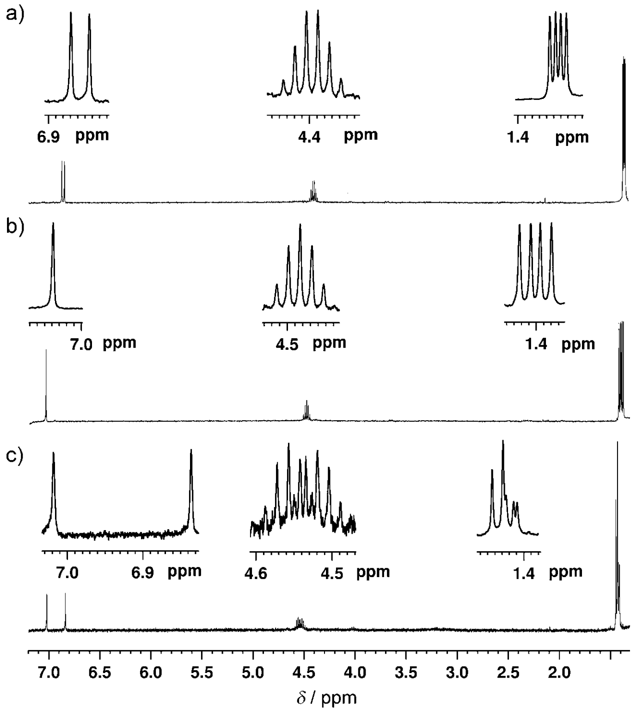

Figure 1. ^{1}H NMR spectra of products **1** (a), **2** (b), and **3** (c).

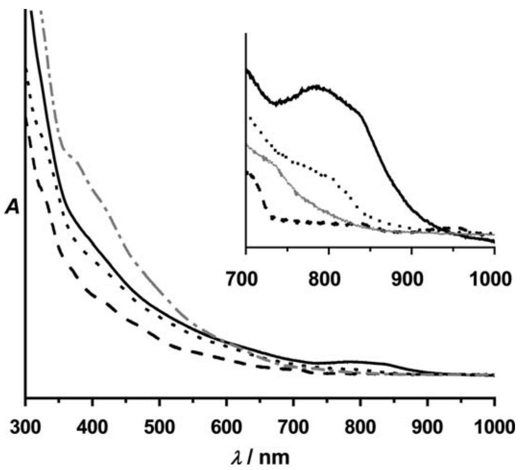

Figure 2. UV/Vis–NIR spectra of products **1**–**3** along with I_h-$Sc_3N@C_{80}$ in toluene. Inset: Expansion of NIR region. —— product **1**, – – – product **2**, ----- product **3**, –•–• I_h-$Sc_3N@C_{80}$.

The ^{1}H NMR spectrum of **3** showed a complex multiplet at $\delta = 4.48$–4.58 ppm for the methine group and three doublets at $\delta = 1.44$, 1.422, and 1.417 ppm for the four methyl groups. Therefore, **3** had no molecular symmetry, and it was difficult to determine where the oxygen atom was located from the ^{1}H NMR data. The UV/Vis-NIR spectrum of **3** exhibited peaks at $\lambda = 336$, 422, and 800 nm, which were different from those of **1** and **2** and also from I_h-$Sc_3N@C_{80}$. To our great satisfaction, the structure of product **3** was unequivocally established by X-ray single-crystal analysis (Figure 3), which showed an unprecedented open-cage structure.

The structure of one enantiomer of compound **3** as determined by X-ray crystallography is shown in Figure 3. Additions of both a benzyne unit and an oxygen atom have occurred at [5,6] ring junctions in a single pentagon.

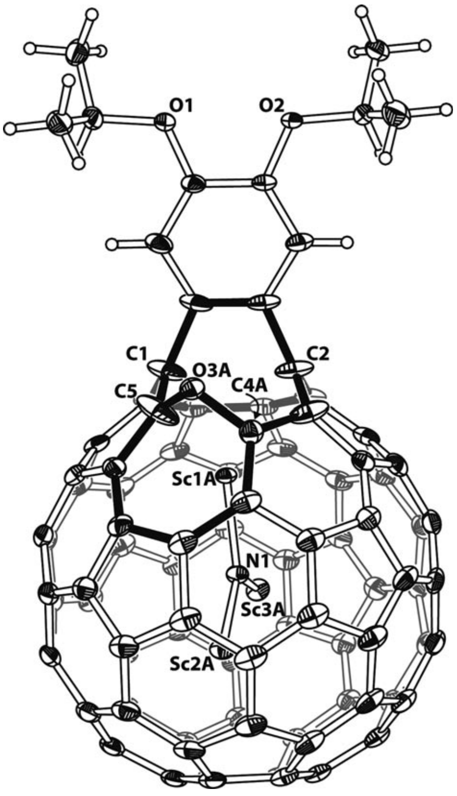

Figure 3. The structure of one enantiomer of product **3** as determined by X-ray crystal crystallography . Ellipsoids are set at 50% probability; disordered atoms O3B and C4B, which produce the other enantiomer, are not shown. Only the major site (0.67 fractional occupancy) for the Sc_3N unit is shown.

Several aspects of the structure are remarkable. An oxygen atom has added to the cage and the C–C bond at the addition site is broken. Thus, the non-bonded C4A···C5 distance is 2.023(5) Å, while the C4A–O3A and C5–O3A bonds lengths are 1.400(4) and 1.324(4) Å. While empty cage fullerenes are known to form adducts with oxygen atoms and to be sensitive to attack by oxidants such as O_2,[6] much less is known about the ability of EMFs to undergo oxygenation.

The C–C bond of the fullerene at the site of benzyne addition is also broken. In other cases of benzyne addition to empty cage fullerenes and to endohedral fullerenes, the cage C–C bond has remained intact.[5a,c] However, in compound **3**, the C1···C2 distance is 2.567(4) Å, whereas the length of normal C–C bond at a [5,6] ring junction is 1.437(15) Å and the length of the corresponding C–C bond in the benzyne adduct, $Sc_3N@I_h\text{-}C_{80}(C_6H_4)$-([5,6]-isomer), is 1.650(2) Å.[5a] As compound **2** appears to be structurally analogous to the previously reported $Sc_3N@I_h\text{-}C_{80}(C_6H_4)$-([5,6]-isomer) with an intact C–C bond at the addition site, it appears that the breaking of the C–C bond at the site of benzyne addition is intimately connected to the addition of the oxygen atom. The ability of one addition reaction to alter the structural characteristics of another portion of the molecule in this case is quite unusual.

As a result of the ruptures of two C–C bonds in the C_{80} cage, an orifice involving a 13-membered ring has been created on the fullerene surface, but that opening is spanned by the oxygen atom and by the benzyne addend. Figure 4 shows a portion of product **3** that surrounds this opening. As shown in Scheme 1, comparison of the structures of the simple benzyne adduct, $Sc_3N@I_h\text{-}C_{80}(C_6H_4)$-([5,6]-isomer), where two of the scandium atoms lie near the *para*-carbon atoms in the six-membered rings adjacent to the site of addition,[5a] and compound **3** reveals that the positions of the scandium atoms have moved so that in **3**, Sc1 A is located near the orifice that has formed. Thus, Sc1 A lies close to four of the carbon atoms in this 13-membered ring. The relevant Sc–C distances are Sc1A–C1 2.474(3), Sc1A–C5 2.444(4), Sc1A–C9 2.356(2), and Sc1A–C10 2.489(3) Å. Despite the high affinity of scandium for oxygen, the oxygen atom protrudes away from the cage and is too far from the scandium atom (Sc1A···O3A distance 3.271(3) Å) to be bonded to it.

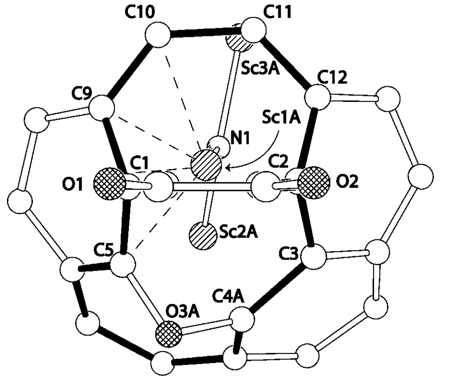

Figure 4. A view of the local environment of the 13-membered ring in product **3** that shows the location of Sc1A near the orifice. The disordered atoms O3B and C4B are not shown.

As seen in Scheme 1, there are two sites, a and b, in compound **2** where an oxygen atom can be added to form compound **3**. Addition at one site produces one enantiomer of **3**, while addition at the second site forms the other enantiomer. As the crystal of **3** is centrosymmetric, it contains a racemate. There is some disorder in the structure. Along with the atoms shown in Figure 3, there are two alternate positions for the Sc_3N group, alternate positions for atoms (O3B and C4B) at the site of oxygen addition, and disorder at the sites of the solvate molecules.

Open-cage fullerenes are known,[7] yet our case, where an open structure is produced instead of a closed four-membered ring, has not been previously described. Existing examples of the opening of three-membered rings include fulleroids, azafulleroids, and oxofulleroids. Fulleroids (methano-bridged annulene-type structures)[8] and azafulleroids (aza-bridged annulene-type structures)[9] may be obtained by thermal extrusion of N_2 from fulleropyrazolines and fullerotriazolines. Fulleroids were alternatively generated via [4+4] intramolecular cycloaddition reactions followed by a retro [2+2+2] ring-opening of the fullerene framework.[10] The addition of carbenes to metallofullerenes[1b,11] and C_{70}[12] also resulted in the formation of fulleroids. Furthermore, the manganese(III) acetate-mediated radical reaction of I_h-$Sc_3N@C_{80}$[2g] and Bingel reaction[3c] of I_h-$Y_3N@C_{80}$ led to metallofulleroids.

The simplest oxofulleroids (oxido-bridged annulene-type structures) $C_{60}O$ and $C_{70}O$ attained from the photolysis of the closed [6,6]-ozone adducts of fullerenes were also reported.[13] However, in all of the above-mentioned fulleroids, azafulleroids, and oxofulleroids there was only one atom, not two as in our case, bridging the broken σ bond in the fullerene skeleton. Furthermore, **3** (with two successively broken bonds in the fullerene skeleton) has the largest orifice among known metallofullerene derivatives, as only one bond is broken in previously reported metallofullerenes.[1b,2g,k,3c,11]

The open-cage metallofullerene **3** could not be isolated under an argon atmosphere, and the yield of **1** was essentially the same under both argon and air atmosphere, indicating that **1** was stable under our reaction conditions, and **3** was generated from further transformation of the [5,6]-regioisomer **2**, not from the [6,6]-regioisomer **1**. Similarly, the reaction of C_{60} with 4,5-diisopropoxybenzyne generated in situ from 2-amino-4,5-diisopropoxybenzoic acid and isoamyl nitrite in air did not afford the oxygenated product, probably because the C_{60}-4,5-diisopropoxybenzyne adduct was a [6,6]-isomer. Furthermore, both **1** and **2** were stable in air at 60 °C for 12 h as well as at 180 °C for 8 h. As found in a related study,[5a] no decomposition or interconversion was observed. The study on the detailed reaction mechanism for the conversion of **2** to **3** is underway. There have been only a limited number of reports on reactions of EMFs with dioxygen. Exposure of solid phases of $M@C_{60}$ (M = Ca, Sr, La, Gd) to air was reported to lead to the destruction of the endohedral and the formation of metal oxides and carbonates.[14] Mass spectroscopic studies of a film of $La@C_{82}$ that had been exposed to air presented evidence for the formation of $La@C_{82}O$ and $La@C_{80}O$.[15] As far as we know, no other oxygen atom adduct of an EMF has been structurally characterized.

In summary, we have investigated the [2+2] cycloaddition reaction of I_h-$Sc_3N@C_{80}$ with 4,5-diisopropoxybenzyne generated in situ. Under an aerobic atmosphere, oxygenation occurred to produce an intriguing open-cage metallofullerene with the largest orifice yet encountered for a metallofullerene, but the reaction gave only the expected [2+2] benzyne adducts under an inert atmosphere. The open-cage product was produced from further reaction of the [5,6]-regioisomer. The present work should stimulate further studies on open-cage metallofullerenes with large orifices, which may exhibit interesting properties, and on the reactivity of endohedral fullerenes with oxygen atom sources.[7]

Experimental Section

General procedure for the reaction of I_h-$Sc_3N@C_{80}$ with 2-amino-4,5-diisopropoxybenzoic acid and isoamyl nitrite: A mixture of I_h-$Sc_3N@C_{80}$ (7.1 mg, 6.4 μmol, synthesized and isolated according to a previous procedure[16]) and 2-amino-4,5-diisopropoxybenzoic acid (8.1 mg, 32.0 μmol) in 1,2-dichlorobenzene (ODCB; 4 mL) was heated at 60 °C under an argon atmosphere; isoamyl nitrite (5.2 μL, 38.4 μmol) was then added by syringe. After being stirred at 60 °C for 12 h, the reaction mixture was separated by flash chromatography on silica gel with carbon disulfide as the eluent to give the first unreacted I_h-$Sc_3N@C_{80}$ fraction (3.4 mg, 48 %) and then a mixture of adducts **1** and **2** (2.4 mg, 29 %). The same reaction with I_h-$Sc_3N@C_{80}$ (7.1 mg, 6.4 μmol), 2-amino-4,5-diisopropoxybenzoic acid (8.1 mg, 32.0 μmol), isoamyl nitrite (6.9 μL, 51.0 μmol), and water (2.9 μL, 161 μmol) in dry ODCB under an air atmosphere afforded unreacted I_h-$Sc_3N@C_{80}$ (3.3 mg, 46 %) and a mixture of products **1**–**3** (1.8 mg, 22 %). The mixture of adducts **1** and **2** as well as that of adduct **1**–**3** was further separated by recycling HPLC on a Cosmosil Buckyprep column (10 mm inside diameter × 250 mm, $T = 40$ °C) with use of toluene (5 mL min^{-1}) as the mobile phase.

Crystal data for $C_{92}H_{16}O_3NSc_3{\cdot}2.5(CS_2)$ (**3**): Crystals were grown by evaporation of a carbon disulfide solution of the adduct **3**. Black needles, $0.16 \times 0.03 \times 0.02$ mm^3, monoclinic, space group $P2_1/n$, $a = 11.0171(9)$, $b = 32.739(3)$, $c = 14.7971(11)$ Å, $\beta = 92.2780(10)$, $V = 5333.0(7)$ Å, $\lambda = 0.77490$ Å, $Z = 4$, $\rho_{calcd} = 1.879$ Mg m^{-3}; $\mu = 0.642$ mm^{-1}; $T = 100(2)$ K; ALS Beamline 11.3.1 Bruker Apex II CCD detector; ω scans, $2\Theta_{max} = 66.26$; 115 804 reflections collected; 15 655 independent ($R_{int} = 0.066$) included in the refinement; min/max transmission = 0.90/0.99 (SADABS-2008/2);[17] Direct methods solution (SHELXS97);[18] full-matrix least-squares based on F^2 (SHELXL97);[18] $R = 0.080$, $wR = 0.140$ for all data; conventional $R1 = 0.052$ computed for 11 499 observed data ($I > 2\sigma(I)$) with 1044 parameters and 8 restraints.

CCDC 808107 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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