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Article

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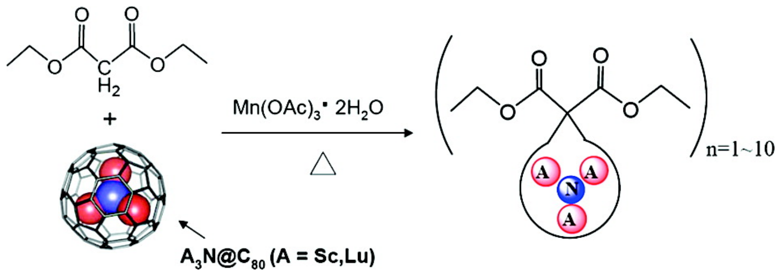

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Manganese(III)-Catalyzed Free Radical Reactions on Trimetallic Nitride Endohedral Metallofullerenes

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Abstract: The first reactions of trimetallic nitride templated endohedral metallofullerenes (TNT EMFs) with carbon radicals generated from diethyl malonate catalyzed by manganese(III) acetate are reported. Two methano monoadducts, $Sc_3N@C_{80}$-**A** and $Sc_3N@C_{80}$-**B**, were isolated and characterized. $Sc_3N@C_{80}$-**A** contains two ester moieties, whereas $Sc_3N@C_{80}$-**B** contains only one ester group and a hydrogen atom on the central carbon of the addend. NMR spectroscopy of the two monoadducts suggests that the addition occurs regioselectively at a 6,6-ring juncture on the surface of the icosahedrally (I_h) symmetric $Sc_3N@C_{80}$, forming the first 6,6-ring-bridged methano I_h $Sc_3N@C_{80}$ derivatives. The measured ${}^1J_{(C,H)} = 147$ Hz for the methano carbon with its hydrogen in monoadduct $Sc_3N@C_{80}$-**B** nearly perfectly matches the data for π-homoaromatic systems, indicating an open [6,6]-methano structure. Geometry optimization also found that the "closed" [6,6]-methano structures were energetically unstable and always led to the open forms. Thus, an "open" [6,6]-methanofulleride structure is proposed, which was induced by the norcaradiene rearrangement, resulting in the cleavage of the cyclopropane ring and the formation of energetically stable open cage fullerene derivatives. These are the first examples of thermodynamically stable adducts of the "open" type at the 6,6-ring juncture of I_h $Sc_3N@C_{80}$, differing greatly from the "closed" 5,6-ring juncture adducts reported previously. In addition, bis-, tri-, and up to octaadducts of $Sc_3N@C_{80}$ were detected by matrix-assisted laser desorption ionization time-of-flight mass spectrometry; this synthetic method was also applied to $Lu_3N@C_{80}$, producing adducts with up to 10 substituents on the carbon cage. These are the highest levels of substitution of TNT metallofullerenes reported so far.

Introduction

Endohedral metallofullerenes (EMFs)[1] are constructed by encapsulating one or more metal atoms in fullerene cages. Generally, EMFs can be classified as classical metallofullerenes (various mono- and di-metallofullerenes),[1,2] metal carbide endohedral fullerenes,[3,4] and trimetallic nitride templated (TNT) metallofullerenes.[5] Since the incarcerated metal atoms imbue EMFs with unusual properties, greatly different from empty fullerenes, the study of EMFs quickly became an active research area.[6−8] Recent research on functionalized EMFs shows promising results for nanomaterials and biomedical applications.[9−18] However, only a limited number of reactions of EMFs to alter the exohedral character and physical properties have been investigated so far, such as [1 + 2] cycloadditions,[19−21] Bingel reactions,[16,22,23] [2+2] cycloadditions,[24] [3+2] cycloadditions,[25−32]

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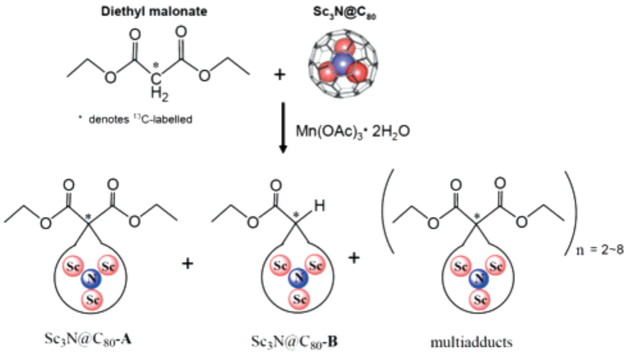
Prato reactions,[22,33−39] [4 + 2] Diels−Alder type cycloadditions,[40−43] and some noncycloadducts.[44−49] Notably, the TNT metallofullerenes,[5] formed in relatively high yields, lower only than C_{60} and C_{70} in the electric-arc Krätschmer−Huffman generator, possess a closed-shell electronic structure and hence are less reactive than classical EMFs. Thus, some methods effective for functionalization of fullerenes and classical metallofullerenes do not work on TNT EMFs, e.g., the normal Bingel reaction fails with I_h $Sc_3N@C_{80}$.[22] Only a few types of reactions effective on the TNT EMFs have been reported so far.[22,23,34,37,40,50] This greatly restricts the range of potential applications for these novel materials. Exploring new ways to functionalize TNT metallofullerenes, especially the formation of highly substituted derivatives, is crucial for expanding their potential applications.

Free radicals are effective intermediates for fullerene functionalization.[51] Manganese(III) acetate is capable of abstracting a hydrogen radical from active methylene compounds to form carbon radicals that can add to alkenes and alkynes.[52−55] By this reaction, many useful compounds have been synthesized.[56−62]

Scheme 1. Synthesis of Mono- and Multiadducts of $Sc_3N@C_{80}$



Notably, Wang and co-workers reported the synthesis of C_{60} dimers in toluene and 1,4-adducts in chlorobenzene using this method.[61,62] Methanofullerenes were obtained only with cyano-substituted malonates.[61]

In the present paper, methano-$Sc_3N@C_{80}$ derivatives were for the first time synthesized via malonate free radicals catalyzed by manganese(III) acetate; these products are completely different from those obtained via thermal addition of diazo compounds,[63−65] addition of free carbenes,[21] and Bingel reactions.[48] Herein, two monoadducts, bis-, tri-, and up to octaadducts of $Sc_3N@C_{80}$ were obtained. This free radical reaction also was applied to functionalization of $Lu_3N@C_{80}$, producing up to decaadducts.

Results and Discussion

Synthesis of Diethyl Malonate Derivatives of $Sc_3N@C_{80}$. To investigate the reaction site and the symmetry of the products,

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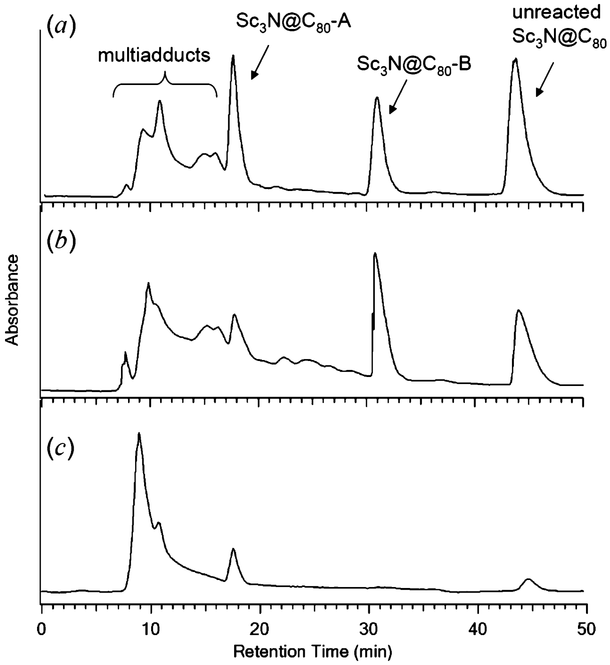


Figure 1. HPLC profiles of reaction mixtures at feed ratios of $Sc_3N@C_{80}$/diethyl malonate/$Mn(OAc)_3\cdot 2H_2O$ of (a) 1:7:75 for 14 h; (b) 1:7:75 for 18 h; (c) 1:30:30 for 14 h. HPLC conditions: 10 mm × 250 mm PYE, flow rate 2 mL/min, toluene as eluent.

an excess of ^{13}C-labeled diethyl malonate (7-fold) and $Mn(OAc)_3\cdot 2H_2O$ (75-fold) were added to $Sc_3N@C_{80}$ in chlorobenzene (Scheme 1). The mixture was refluxed under the protection of N_2 for 14 h. After the reaction, the solvent was evaporated and the residue was dissolved in toluene and analyzed by HPLC. The HPLC profile of the reaction mixture (Figure 1a) shows two major product peaks centered at retention times of 17.6 min (designated $Sc_3N@C_{80}$-**A**) and 31.0 min (designated $Sc_3N@C_{80}$-**B**), together with some lower elution time products. $Sc_3N@C_{80}$-**A** and $Sc_3N@C_{80}$-**B** were easily separated from other adducts and unreacted starting materials by HPLC (Figure 2, parts b and a). Positive-ion matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra of $Sc_3N@C_{80}$-**A** and $Sc_3N@C_{80}$-**B** exhibit strong molecular ion peaks at *m*/*z* 1269 and 1197, respectively (Figure 3, parts b and a), accounting for the production of two monoadducts $Sc_3N@C_{80}[^{13}C(COOC_2H_5)_2]$ (**A**) and $Sc_3N@C_{80}[^{13}CHCOOC_2H_5]$ (**B**). The peak at *m*/*z* 1110 is attributed to $Sc_3N@C_{80}$ formed by loss of the exohedral functional groups $[^{13}C(COOC_2H_5)_2]$ and $[^{13}CHCOOC_2H_5]$ from $Sc_3N@C_{80}$-**A** and $Sc_3N@C_{80}$-**B**, respectively, under the laser desorption.[50] Notably, a peak at *m*/*z* 1125 was detected, which can be ascribed to $Sc_3N@C_{80}-{}^{13}CH_2$, indicating that the methano carbon attached on the carbon cage can endure the laser desorption process. With increased reaction time, the yield of $Sc_3N@C_{80}$-**B** increased relative to $Sc_3N@C_{80}$-**A** (Figure 1b), suggesting that $Sc_3N@C_{80}$-**A** evolves into $Sc_3N@C_{80}$-**B** and $Sc_3N@C_{80}-CH_2$ via transesterification and decarboxylation reactions (see below). When the feed ratio of $Sc_3N@C_{80}$, diethyl malonate, and $Mn(OAc)_3\cdot 2H_2O$ was changed to 1:30:30, the yield of multiadducts at shorter elution times increased relative to $Sc_3N@C_{80}$-**A** and $Sc_3N@C_{80}$-**B** (Figure 1c). Bisadducts and triadducts of $Sc_3N@C_{80}$ at retention times of 11.5 min and 10.0 min were also isolated (Figure 2, parts c and d) and confirmed by MALDI-TOF MS (Figure 3, parts c and d). In addition, octaadducts of $Sc_3N@C_{80}$ were detected (Figure 3e) in a mixture of multiadducts with much lower retention time, 8.7 min (Figure 2e). We also tried the same conditions applied to C_{60},[61] i.e., treating $Sc_3N@C_{80}$ with 2 equiv of diethyl malonate and 2 equiv of $Mn(OAc)_3\cdot 2H_2O$ in refluxing chlorobenzene for different reaction times. The results indicated that reducing the dose of diethyl malonate and $Mn(OAc)_3\cdot 2H_2O$ and shortening reaction time not only did not lead to analogues of the C_{60} products but also reduced the conversion of $Sc_3N@C_{80}$.

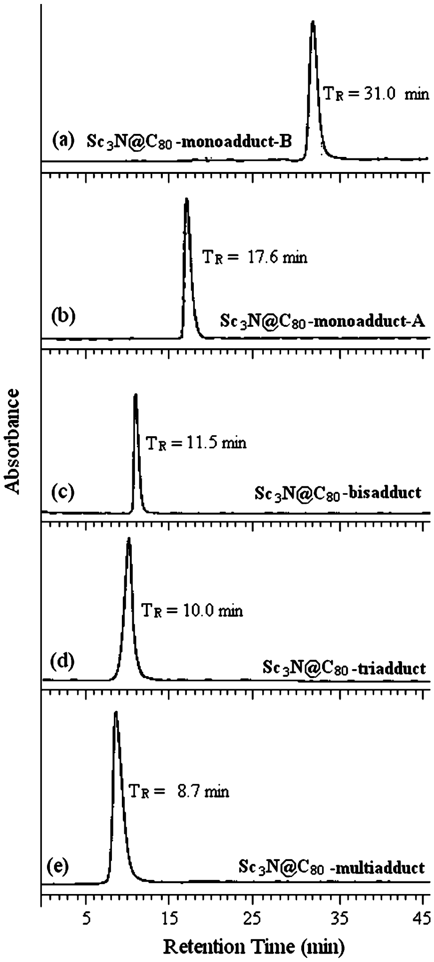


Figure 2. HPLC profiles of pure products (a) $Sc_3N@C_{80}$-monoadduct-**B**, (b) $Sc_3N@C_{80}$-monoadduct-**A**, (c) $Sc_3N@C_{80}$-bisadducts, (d) $Sc_3N@C_{80}$-triadducts, and (e) $Sc_3N@C_{80}$-multiadducts. HPLC conditions: 10 mm × 250 mm PYE at a flow rate of 2 mL/min with toluene as eluent.

Structure Determination of Diethyl Malonate Derivatives of $Sc_3N@C_{80}$. There are two reaction sites on the I_h $Sc_3N@C_{80}$ cage. One is the corannulene-type site, a double bond at a 5,6-ring junction abutted by two hexagons (Scheme 2, **A** or **B**); the other is the pyrene-type site, a double bond at a 6,6-ring junction abutted by a hexagon and a pentagon (Scheme 2, **C** or **D**). Interestingly, cycloaddition reactions on I_h $Y_3N@C_{80}$ are regioselective for a pyrene-type site,[22] whereas with $Sc_3N@C_{80}$ similar reactions have always occurred regioselectively at a corannulene-type site[22,37] except for a kinetically favored 6,6-juncture adduct.[50]

NMR and X-ray crystallography are effective tools for structural characterization of EMFs.[23,47,50] Herein, we use NMR to characterize the first methano-TNT derivatives obtained via free radical reactions. Scheme 2 demonstrates that addition at the 5,6-ring junction will cause the two ethyl groups be

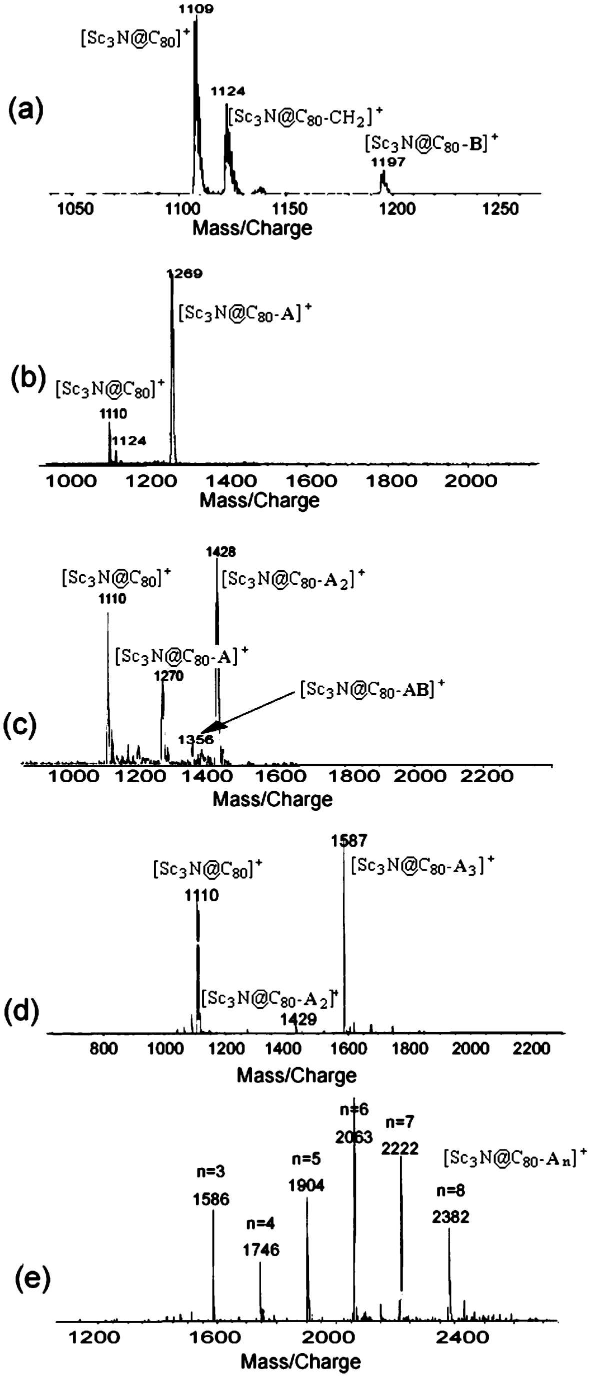


Figure 3. Positive-ion mode MALDI-TOF mass spectra of (a) $Sc_3N@C_{80}$-**B**, (b) $Sc_3N@C_{80}$-**A**, (c) $Sc_3N@C_{80}$-bisadducts, (d) $Sc_3N@C_{80}$-triadducts, and (e) up to $Sc_3N@C_{80}$-octaadducts using a 9-nitroanthracene matrix; **A** and **B** represent exohedral functional groups [$^{13}C(COOC_2H_5)_2$] and [^{13}-$CHCOOC_2H_5$], respectively.

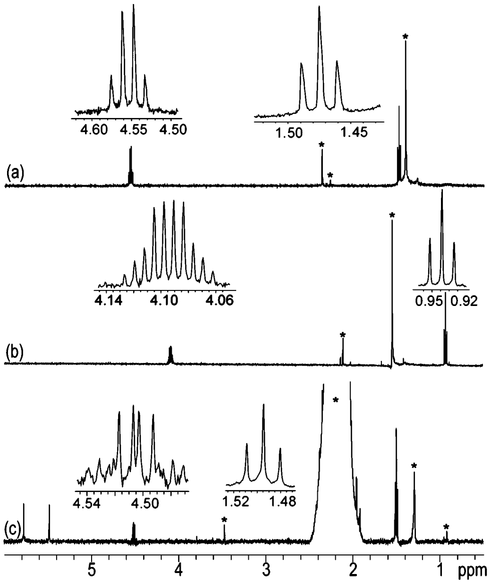


Figure 4. 500 MHz ^1H NMR spectra of $Sc_3N@C_{80}$-**A** in (a) chloroform-*d*/CS_2 (v/v = 30/70) and (b) benzene-d_6; $Sc_3N@C_{80}$-**B** in (c) acetone-d_6/CS_2 (v/v = 10/90). * denotes impurity from the solvent.

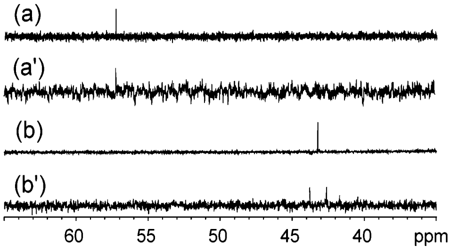


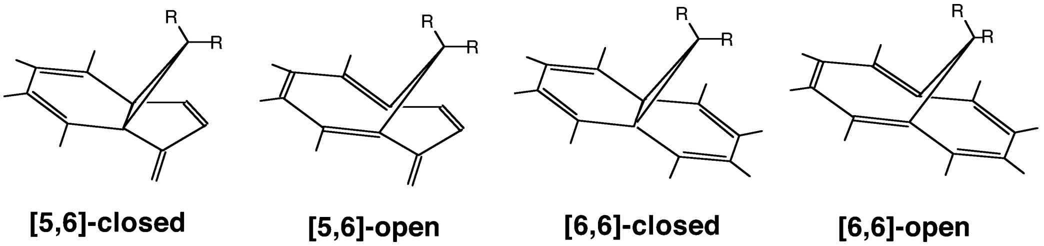
Figure 5. ^{13}C NMR (125 MHz, acetone-d_6/CS_2 = 10/90) spectra: (a), (a′), (b), and (b′) are decoupled and coupled spectra of ^{13}C-labeled $Sc_3N@C_{80}$-**A** and $Sc_3N@C_{80}$-**B**, respectively.

nonequivalent (Scheme 2, **A** and **B**), but addition at the 6,6-ring junction will produce equivalent ethyl moieties (Scheme 2, **C** or **D**).[22] In the ^1H NMR spectrum of $Sc_3N@C_{80}$-**A** in chloroform-*d*/CS_2 (v/v = 30/70) (Figure 4a), one set of signals at 4.55 and 1.47 ppm was observed, accounting for the presence of equivalent ethyl groups. Thus, addition at a 5,6-ring junction (Scheme 2, **A** or **B**) in $Sc_3N@C_{80}$-**A** was ruled out.[22,50] Interestingly, though the ^1H NMR spectrum of $Sc_3N@C_{80}$-**A** in C_6D_6 (Figure 4b) exhibits one set of signals at 4.10 and 0.94 ppm, the multiplet for the diastereotopic methylene protons is obvious and the ethyl protons are shifted upfield due to the ring current effect of C_6D_6.

Likewise, the ^1H NMR spectrum of $Sc_3N@C_{80}$-**B** in acetone-d_6/CS_2 (v/v = 10/90) (Figure 4c) exhibits one set of signals at similar positions, 4.51 and 1.50 ppm, respectively, for its ethyl groups, suggesting that addition also occurs at the 6,6-ring junction (Scheme 2, **C** or **D**). Notably, the signal for the methylene protons consists of a more complex pattern, typical of overlapping peaks from diastereotopic methylene hydrogens. Besides the signals of the ethyl group, $Sc_3N@C_{80}$-**B** displays two proton peaks with the same intensity centered at 5.77 and 5.48 ppm. Considering the possible composition of the ^{13}C-labeled derivatives, the two signals must be derived from coupling of a hydrogen bonded with a ^{13}C-labeled carbon ($^1J_{C-H}$ = 147 Hz). To confirm this, decoupled and coupled ^{13}C NMR spectra along with heteronuclear multiple quantum coherence (HMQC) spectroscopic experiments were conducted on the two compounds.

As parts a and a′ of Figure 5 show, both the decoupled and coupled ^{13}C NMR spectra of $Sc_3N@C_{80}$-**A** exhibit a singlet at 57.3 ppm, indicating a quarternary carbon with no proton attached. Moreover, the HMQC spectrum of $Sc_3N@C_{80}$-**A** does not exhibit any correlation between the ^{13}C carbon and protons, further confirming that no proton is linked to the ^{13}C-labeled carbon of $Sc_3N@C_{80}$-**A**. In contrast, the decoupled ^{13}C NMR spectrum of $Sc_3N@C_{80}$-**B** (Figure 5b) exhibits one signal at 43.2

Scheme 2. Possible Cycloaddition Products of I_h $Sc_3N@C_{80}$, Reading from Left to Right: [5,6]-Closed Adduct (**A**), [5,6]-Open Adduct (**B**), [6,6]-Closed Adduct (**C**), and [6,6]-Open Adduct (**D**)[a]



[a] Because of symmetry differences, the ethyl moieties (R) are nonequivalent in **A** and **B**, but equivalent in **C** and **D**.

ppm, whereas the coupled ^{13}C NMR spectrum (Figure 5b′) shows a doublet at 43.2 ppm with $^1J_{C-H} = 147$ Hz, indicating a hydrogen attached to the ^{13}C carbon of $Sc_3N@C_{80}$-**B**. The HMQC spectrum of $Sc_3N@C_{80}$-**B** confirms the $^{13}C-^1H$ correlation, further verifying the existence of a hydrogen attached to the methano carbon. These results are completely consistent with the diastereotopic nature of the methylene protons in $Sc_3N@C_{80}$-**B**. Thus, methano-bridged $Sc_3N@C_{80}$ derivatives rather than noncycloadducts[48] were obtained.

Recently, Echegoyen's group reported a 6,6-juncture methano derivative of I_h $Y_3N@C_{80}$ via a classical Bingel reaction, but the same reaction failed with I_h $Sc_3N@C_{80}$.[22] The ^1H NMR spectrum of the "cyclopropanation" product of I_h $Y_3N@C_{80}$ in C_6D_6 exhibits signals at 1.05 ppm (t, CH_3, 2H, $J = 7.1$ Hz) and 4.22 ppm (q, CH_2, 2H, $J = 7.1$ Hz).[22] Similarly, in the present work $Sc_3N@C_{80}$-**A** produces sharp and symmetric signals at 1.47 ppm (t, CH_3, 3H, $J = 7.0$ Hz) and 4.55 ppm (q, CH_2, $J = 7.0$ Hz) in $CDCl_3/CS_2$. The downfield shifts in the Sc compound versus the Y compound could be caused by the different encapsulated metals. For $Sc_3N@C_{80}$-**B**, which presumably results from loss of a carboxylate group from $Sc_3N@C_{80}$-**A**, the methylene signal at 4.51 ppm and the methyl signal at 1.49 ppm (t, CH_3, $J = 7.2$ Hz) are shifted only a little (0.02∼0.04 ppm) relative to those of $Sc_3N@C_{80}$-**A**. Thus, the two monoadducts based on $Sc_3N@C_{80}$ are [6,6]-ring-bridged methano products as shown in Scheme 2, **C** or **D**.

Notably, these are the first examples of thermodynamically stable 6,6-juncture adducts of I_h $Sc_3N@C_{80}$. Campanera et al.[66] reported that the planar endohedral Sc_3N cluster of $Sc_3N@C_{80}$ causes a local outward pyramidalization of the C−C cage bonds closest to the scandium nuclei and the coroannulene 5,6-double bonds next to Sc have the highest strain of all the bonds in the I_h C_{80} cage, which makes them the most reactive toward exohedral cycloaddition. Therefore, reaction at a 5,6-double bond can relieve part of the bond strain and produce the thermodynamically more stable adduct, which was corroborated by both Diels−Alder[40] and pyrrolidine adducts[37,38] of $Sc_3N@C_{80}$. However, from our experimental results, 6,6-juncture adducts of methano-bridged $Sc_3N@C_{80}$ seem to be thermodynamically stable species, since they endure reflux at 130 °C for 14 h.

It is well-known that difficulties frequently arise in the characterization of fullerene derivatives, especially for the differentiation of isomers. The differentiation of cyclopropane and [5,6]-open isomers of fullerenes are typical examples.[64,67] Fortunately, scientists have found that the [5,6]-open structure will lead to methanoannulene π-homoaromaticity, and thus the coupling constant $^1J_{(C,H)}$ at the methano bridge C-atom is smaller than that of the [6,6]-closed isomer, since the methanoannulene is σ-homoaromatic; e.g., for the [5,6]-open methanofulleride, $C_{60}[CHCO_2CH_2CH_3]$, the $^1J_{(C,H)}$ at the methano bridge C-atom is 143.6 or 143.0 Hz, whereas that of the [6,6]-closed methanofullerene is 166.1 Hz.[68] In the present study, $Sc_3N@C_{80}$-**B** as an analogue of $C_{60}[CHCO_2CH_2CH_3]$ exhibits a similar coupling constant at the methano bridge C-atom, $^1J_{(C,H)} = 147$ Hz, indicative of an open structure. Likewise, the ^{13}C NMR data are in agreement with an open transannular bond, since the apex carbon signals are shifted downfield (57.3 ppm for $Sc_3N@C_{80}$-**A** and 43.2 ppm for $Sc_3N@C_{80}$-**B**) relative to those of cyclopropyl derivatives.[67] Akasaka's group reported an anion[48] of $La@C_{82}C(COOC_2H_5)_2$ with chemical shift of the methano carbon atom at 65.74 ppm and designated its structure to be the [6,6]-open methano derivative. Very recently, Echegoyen's group reported a Bingel adduct $Y_3N@C_{80}-C(CO_2CH_2Ph)_2$ with chemical shift of the methano carbon at 61.46 ppm, and the X-ray analysis clearly revealed an [6,6]-open structure.[23] Our results are similar to these reported resonances, and thus the products can be considered to be methanofulleroid derivatives.

The electronic absorption spectra of the [5,6]-open structure with π-homoaromaticity and the [6,6]-closed isomer with σ-homoaromaticity are different, since the spherical chromophore of the former is less perturbed than that of the latter.[23,68] The UV−vis spectra of $Sc_3N@C_{80}$-**A** and $Sc_3N@C_{80}$-**B** are similar to their precursor, $Sc_3N@C_{80}$, as shown in Figure 6, indicating that the two monoadducts are fulleroids. Notably, the detection of the $Sc_3N@C_{80}-CH_2$ fragment in the mass spectra (Figure 3, parts a and b) is also consistent with the conclusion that the adducts have "open" structures, since according to our calculations the unsubstituted, "closed" cyclopropyl derivative of $Sc_3N@C_{80}$ is also unstable due to the ring strain.

Furthermore, the "closed" [6,6]-methano structures also proved to be energetically unstable by geometry optimization and always led to the open form. Figure 7 shows the geometrically optimized, thermodynamically stable structure of "open" [6,6]-methanofulleroids $Sc_3N@C_{80}$-**A** and $Sc_3N@C_{80}$-**B**. The C2−C10 distances of $Sc_3N@C_{80}$-**A** and $Sc_3N@C_{80}$-**B** are 2.19(9) and 2.18(9) Å, respectively, whereas the average C−C bond length at a [6,6]-ring junction in $Sc_3N@C_{80}$-I_h is 1.421(18) Å,[41] indicating an elongation of C2−C10 separation in these products. Lukoyanova et al. reported an open malonate methano−fullerene derivative, $Y_3N@C_{80}-C(CO_2CH_2Ph)_2$.[23] In

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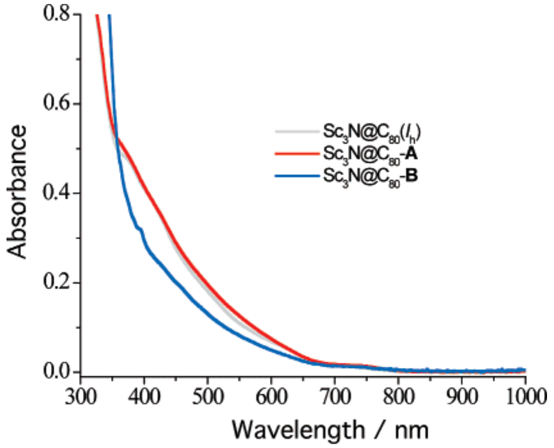

Figure 6. UV−vis spectra of $Sc_3N@C_{80}$-**A** (red line) and $Sc_3N@C_{80}$-**B** (blue line) together with $Sc_3N@C_{80}$ (I_h) (gray line) in toluene.

this material, the crystallographically characterized structure revealed an open [6,6]-ring junction adduct with C1−C9 distances of 2.30(3) Å for one orientation of the cage and 2.28(4) Å in the other orientation. In addition, Maeda et al. reported a modified carbene addition of an adamantylidene moiety to form La@C_{82}-(Ad),[21] in which the opened C−C separation on the [6,6]-ring junction is 2.097 Å. All of the evidence indicates that $Sc_3N@C_{80}$-**A** and $Sc_3N@C_{80}$-**B** are open [6,6] regioisomers. Notably, in the minimized structures Sc1 atoms in $Sc_3N@C_{80}$-**A** and $Sc_3N@C_{80}$-**B** are positioned near the sites of the cleaved bond formerly between C2 and C10 with contact distances of 2.42(9) and 2.51(6) Å for $Sc_3N@C_{80}$-**A**, and 2.43(2) and 2.52(4) Å for $Sc_3N@C_{80}$-**B**, respectively, very similar to those of $Y_3N@C_{80}-C(CO_2CH_2Ph)_2$ (2.47−2.57 Å).[23] The distances between the Sc1 atoms and methano carbons are 3.21(8) and 3.23(4) Å for $Sc_3N@C_{80}$-**A** and $Sc_3N@C_{80}$-**B**, respectively.

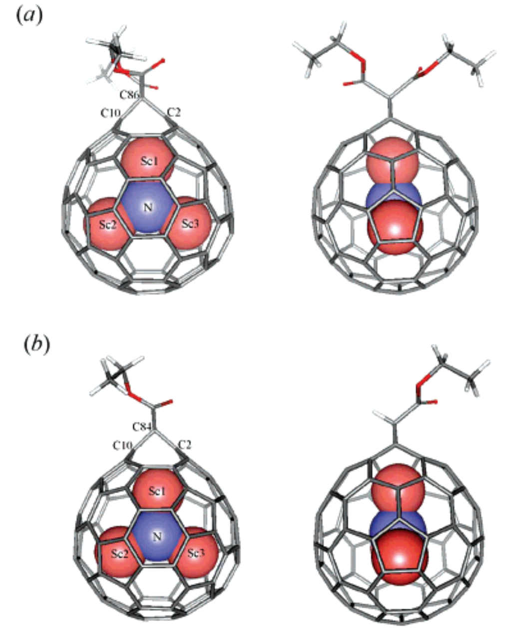

Figure 7. Geometrically optimized, thermodynamically stable structures of "open" [6,6]-methanofullerides (a) $Sc_3N@C_{80}$-**A** and (b) $Sc_3N@C_{80}$-**B**. On the left and right are top and edge-on views relative to the Sc_3N unit, respectively.

DFT calculations revealed higher LUMOs for the [6,6]-open isomers than the corresponding [5,6]-open isomers, leading to larger HOMO−LUMO gaps than their [5,6]-open regioisomers, as shown in Table 1. In addition, the [6,6]-open isomers are highly favored thermodynamically relative to the [5,6]-open isomers for both $Sc_3N@C_{80}$-**A** and $Sc_3N@C_{80}$-**B**, further confirming that the [6,6]-open methano structures are able to relieve the ring strain present in the closed analogues (Scheme 2, **D**).

Scheme 3. (a) Suggested Mechanism for Free Radical Reaction of Diethyl Malonate with $Sc_3N@C_{80}$ Using $Mn(OAc)_3$ as Catalyst, Leading to Product **A** and (b) Proposed Mechanism for Conversion of Product **A** into Product **B** via Transesterification and Decarboxylation

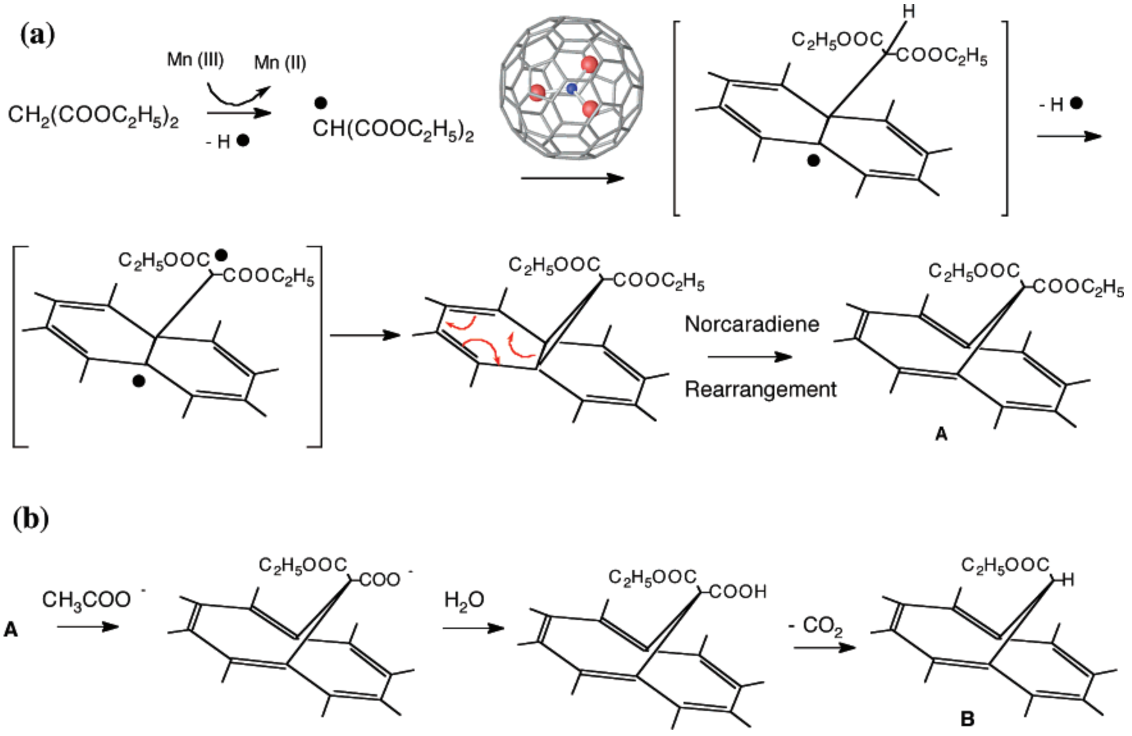

Table 1. HOMO/LUMO Levels (eV) for [5,6]-Open and [6,6]-Open Regioisomers of $Sc_3N@C_{80}$-**A** and $Sc_3N@C_{80}$-**B** and Energy Differences between the Two Isomers

compd		HOMO (eV)	LUMO (eV)	(HUMO–LUMO) (eV)	$\Delta E_{[5,6]-[6,6]}$ (kcal/mol)
$Sc_3N@C_{80}$-**A**	[5,6]-open	−5.824	−3.509	2.315	11.588
	[6,6]-open	−5.742	−3.297	2.445	
$Sc_3N@C_{80}$-**B**	[5,6]-open	−5.779	−3.638	2.141	14.523
	[6,6]-open	−5.818	−3.348	2.470	

According to the experimental observations and the reported function of manganese(III),[52−55] a reaction mechanism is proposed in Scheme 3. First, Mn(III) abstracts a hydrogen radical from the active methylene moiety of diethyl malonate to generate a radical, which subsequently attacks $Sc_3N@C_{80}$ at a 6,6-juncture to form an intermediate containing a free radical on the carbon cage. The excess Mn(III) can abstract another hydrogen radical from the active methylene unit; thus, the resultant diradicals combine to form an unstable intermediate, the cyclopropyl derivative of $Sc_3N@C_{80}$, which will tend to rearrange, resulting in a thermodynamically stable [6,6]-open methanofulleroid ($Sc_3N@C_{80}$-**A**). Interestingly, the proportion of $Sc_3N@C_{80}$-**B** increases with increasing reaction time (Figure 1b), and thus the formation of $Sc_3N@C_{80}$-**B** is believed to be derived from $Sc_3N@C_{80}$-**A** as follows. First, transesterification between $Sc_3N@C_{80}$-**A** and acetate ion from the catalyst leads to formation of the carboxylate derivative of $Sc_3N@C_{80}$-**A**. Second, the water present in the reaction system (again from the catalyst) gives rise to the carboxylic acid derivative of $Sc_3N@C_{80}$-**A**. Third, the unstable carboxylic acid decarboxylates, leading to the formation of $Sc_3N@C_{80}$-**B**. Repetition of these three steps will produce $Sc_3N@C_{80}{-}CH_2$.

Thus $Sc_3N@C_{80}$-**A**, $Sc_3N@C_{80}$-**B**, and $Sc_3N@C_{80}{-}CH_2$ possess the same [6,6]-open methanofulleride structures. In pronounced contrast, the reported fullerene dimers and 1,4-bisadducts of C_{60}[61] were proposed to form by another reaction route, i.e., C_{60} as a good electron acceptor is easily attacked by the radical $\cdot CH(COOC_2H_5)_2$ to form a fullerene radical at the 4-position, which combines with itself or $\cdot CH(COOC_2H_5)_2$ to form the dimer or the 1,4-bisadduct. Whereas the lack of formation of 1,2-adducts is due to strong steric interaction between proximal bulky diethyl malonate moieties, the formation of cyclopropane-fused C_{60} from the cyano-substituted malonate may be due to its smaller steric effect. Therefore, the chemistry of TNT metallofullerenes is distinctly different from that of C_{60} and needs further exploration in order to optimize their properties for various applications.

Synthesis of Derivatives of $Lu_3N@C_{80}$ from Diethyl Malonate. Via the same method with $Lu_3N@C_{80}$ we obtained two monoadducts, which have HPLC retention times similar to those of the analogous $Sc_3N@C_{80}$ monoadducts **A** and **B**. Positive-ion MALDI-TOF MS of the purified monoadducts exhibit strong molecular ion peaks at *m*/*z* 1658 and 1587, respectively (Figure 8, parts a and b), corresponding to $Lu_3N@C_{80}[^{13}C(COOC_2H_5)_2]$ (**A**) and $Lu_3N@C_{80}[^{13}CHCOOC_2H_5]$ (**B**). The peak at *m*/*z* 1514 can be ascribed to $Lu_3N@C_{80}{-}CH_2$, indicating that the two functionalized monoadducts are "open" methanofullerides, probably [6,6]-juncture products. Unexpectedly, up to decaadducts of $Lu_3N@C_{80}$ were detected by MALDI-TOF MS (*m*/*z* 3091, Figure 8c). This is most likely due to the higher reactivity of $Lu_3N@C_{80}$ relative to $Sc_3N@C_{80}$.[34] The multiadducts have good solubility in polar solvents, such as acetone and chloroform.

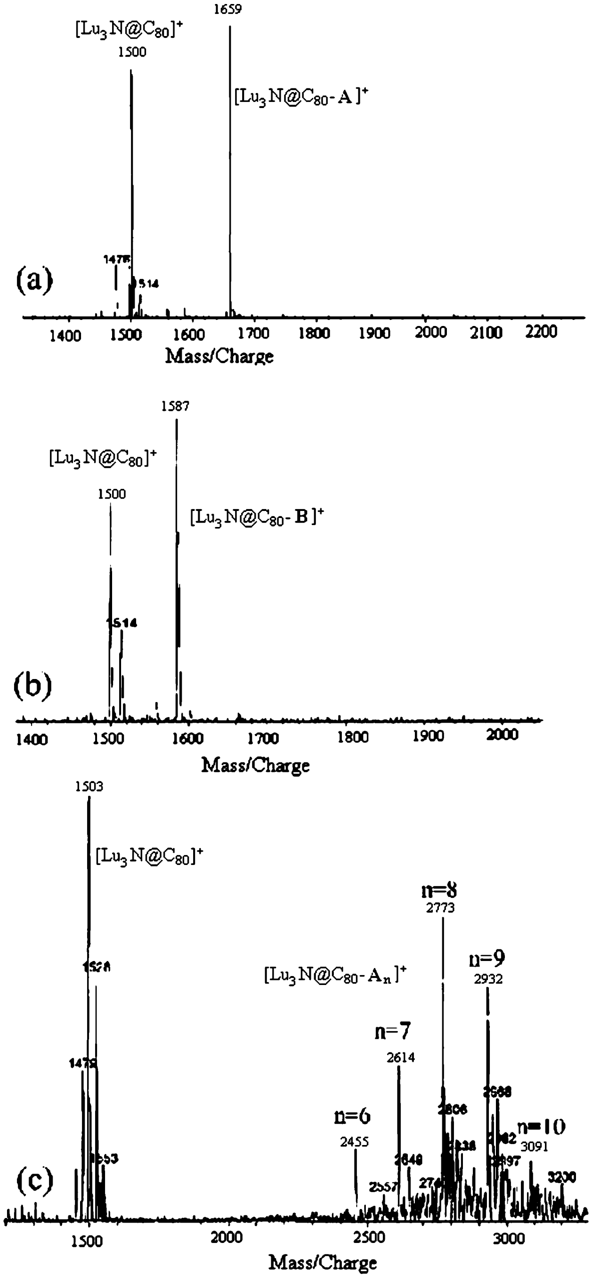

Figure 8. Positive-ion mode MALDI-TOF mass spectra of (a) $Lu_3N@C_{80}$-**A**, (b) $Lu_3N@C_{80}$-**B**, and (c) up to $Lu_3N@C_{80}$-decaadducts using a 9-nitroanthracene matrix.

Conclusions

In conclusion, two methano-bridged monoadducts of I_h $Sc_3N@C_{80}$ were synthesized for the first time via free radical reactions, as proved by MALDI-TOF MS and NMR spectroscopy. The same conditions were successfully applied to $Lu_3N@C_{80}$ to produce similar analogues. Multiadducts with up to 10 methano units were produced from I_h $Sc_3N@C_{80}$ and $Lu_3N@C_{80}$ by controlled reaction conditions. Therefore, the enhanced free radical reaction is destined to be very useful for production of functionalized metallofullerides for potential applications in several areas of technology. This method provides a novel means for the synthesis of functionalized methano-TNT EMFs with all kinds of β-dicarbonyl compounds designed for various applications. NMR data and UV spectra together with geometry optimization suggest that they are the most thermodynamically stable [6,6]-open methanofullerides. For detailed structural characterization, X-ray crystallographic analysis is ongoing.

Experimental Section

Materials and Methods. A I_h and D_{5h} isomer mixture of $Sc_3N@C_{80}$ was obtained by the chemical separation method, as reported in detail earlier.[69] Pure I_h $Sc_3N@C_{80}$ was isolated from the mixture by HPLC using a semipreparative PYE [β-(1-pyrenyl)ethyl silica] column (10 mm × 250 mm) with toluene at 2.0 mL/min, $\lambda = 390$ nm. ^{13}C-labeled diethyl malonate (99%, Cambridge Isotope Laboratory, Inc.) was used to synthesize ^{13}C-enriched monoadducts. Toluene (HPLC grade, $\geq$99.9%), $Mn(OAc)_3{\cdot}2H_2O$, and chlorobenzene were used as received from Aldrich. The same PYE column was also used for both analysis and purification of products. The HPLC system was the following: Acure series III pump, 757 absorbance detector (Applied Biosystems). A JEOL ECP 500 MHz instrument was used for all NMR measurements. Mass spectrometry was conducted on a Kratos Analytical Kompact SEQ MALDI-TOF mass spectrometer. Geometry optimization was explored at the B3LYP level[70] using the Gaussian 03 program.[71] The effective core potential and the corresponding basis set were used for Sc. The basis sets employed were LanL2DZ[71] for Sc and 3-21G*[72] for C, H, O, and N.

Synthesis of Diethyl Malonate Derivatives of $Sc_3N@C_{80}$. A mixture of $Sc_3N@C_{80}$ (0.45 mg, 0.4 μmol), ^{13}C-labeled diethyl malonate (0.48 mg, 3.0 μmol), and $Mn(OAc)_3{\cdot}2H_2O$ (8.04 mg, 30.0 μmol) in 5 mL of chlorobenzene was refluxed under the protection of N_2 for 14 h. The solvent was removed by a rotary evaporator. The residue was dissolved in toluene and injected into an HPLC for analysis. $Sc_3N@C_{80}$-**A**, $Sc_3N@C_{80}$-**B**, and a multiadduct mixture were isolated by HPLC using a PYE column, with toluene at 2.0 mL/min, $\lambda = 390$ nm.

Synthesis of Diethyl Malonate Derivatives of $Lu_3N@C_{80}$. These reactions and purifications were carried out analogously to the procedures outlined above for the derivatives of $Sc_3N@C_{80}$.

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Supporting Information Available: 500 MHz COSY spectra of $Sc_3N@C_{80}$-**A** and $Sc_3N@C_{80}$-**B**, HMQC NMR spectrum of ^{13}C-labeled $Sc_3N@C_{80}$-**B**, HPLC profiles of pure $Lu_3N@C_{80}$-**A** and $Lu_3N@C_{80}$-**B**, geometrically optimized, thermodynamically stable structures of "open" [6,6]-methanofullerides for $Sc_3N@C_{80}$-**A** and $Sc_3N@C_{80}$-**B**, together with optimized *XYZ* coordination, and complete ref 71. This material is available free of charge via the Internet at http://pubs.acs.org.

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