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Synthesis, Isolation, and Addition Patterns of Trifluoromethylated D_{5h} and I_h Isomers of $Sc_3N@C_{80}$: $Sc_3N@D_{5h}$-$C_{80}(CF_3)_{18}$ and $Sc_3N@I_h$-$C_{80}(CF_3)_{14}$

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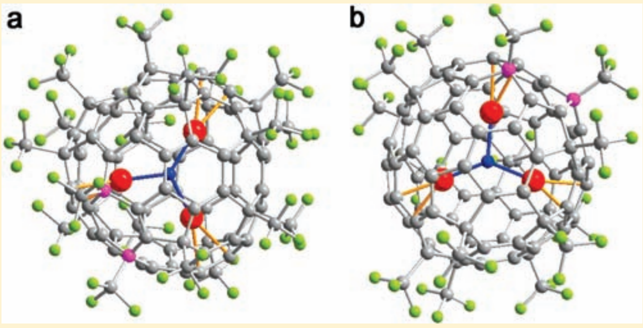
Supporting Information

ABSTRACT: $Sc_3N@D_{5h}$-C_{80} and $Sc_3N@I_h$-C_{80} were trifluoromethylated with CF_3I at 400 °C, affording mixtures of CF_3 derivatives. After separation with HPLC, the first multi-CF_3 derivative of $Sc_3N@D_{5h}$-C_{80}, $Sc_3N@D_{5h}$-$C_{80}(CF_3)_{18}$, and three new isomers of $Sc_3N@I_h$-$C_{80}(CF_3)_{14}$ were investigated by X-ray crystallography. The $Sc_3N@D_{5h}$-$C_{80}(CF_3)_{18}$ molecule is characterized by a large number of double C—C bonds and benzenoid rings within the D_{5h}-C_{80} cage and a fully different position of the Sc_3N unit compared to that in the pristine $Sc_3N@D_{5h}$-C_{80}. A detailed comparison of five $Sc_3N@I_h$-$C_{80}(CF_3)_{14}$ isomers reveals a strong influence of the exohedral additions on the behavior of the Sc_3N cluster inside the I_h-C_{80} cage.



INTRODUCTION

Metal nitride clusterfullerenes (NCFs) have been attracting considerable attention in the past decade due to their interesting properties and prospective applications in biomedicine and nanomaterial sciences.[1] X-ray crystallography has been extensively used to determine the molecular structures of NCFs since the discovery of $Sc_3N@I_h$-C_{80}.[1,2] Typically, a Sc_3N unit within $Sc_3N@C_{80}$ undergoes rapid reorientation relative to the C_{80} cage, and this phenomenon was observed in different solvates, including cocrystals of $Sc_3N@I_h$-C_{80} with metal octaethylporphyrins (OEPs).[2a,c] In contrast, no orientational disorder of both the D_{5h}-C_{80} cage and the Sc_3N unit was found for cocrystals of $Sc_3N@D_{5h}$-C_{80} with nickel octaethylporphyrin.[3]

Exohedral functionalization of NCFs has great significance toward their potential applications.[4] Among them, trifluoromethylation of $Sc_3N@C_{80}$ was recently accomplished in a few reports, affording $Sc_3N@C_{80}(CF_3)_n$ ($n = 2-16$).[5−7] As the first example, $Sc_3N@C_{80}(CF_3)_2$ was synthesized by a flow reaction of gaseous CF_3I with either pure $Sc_3N@I_h$-C_{80} or a mixture of I_h and D_{5h} isomers of $Sc_3N@C_{80}$. The synthesized $Sc_3N@I_h$-$C_{80}(CF_3)_2$ was characterized by ^{19}F NMR, electrochemistry, and UV—vis spectroscopy, whereas the corresponding $Sc_3N@D_{5h}$-$C_{80}(CF_3)_2$ was not isolated in the pure form.[5] A family of $Sc_3N@C_{80}(CF_3)_n$ ($n = 2-16$) was synthesized using a high-temperature reaction of $Sc_3N@C_{80}$ with silver trifluoroacetate, $Ag(CF_3CO_2)$, in a sealed tube. After isolation by HPLC, some compounds were characterized by different methods, including ^{19}F NMR and X-ray crystallography (four isomers with $n = 10, 12, 14$, and 16). Some general principles of addition patterns in $Sc_3N@C_{80}(CF_3)_n$ were formulated.[6] Recently, we synthesized two new isomers of $Sc_3N@C_{80}(CF_3)_{14,16}$ by an ampule reaction of $Sc_3N@I_h$-C_{80} with CF_3I, and a strong influence of the exohedral CF_3 addition pattern on the behavior of Sc_3N cluster inside the I_h-C_{80} cage was concluded.[7] It is noteworthy that these studies of multi-CF_3 derivatives of $Sc_3N@I_h$-C_{80} revealed a high degree of order for both the I_h-C_{80} cage and the Sc_3N unit,[6,7] which is in marked contrast to the case of the pristine $Sc_3N@I_h$-C_{80}.[2a,c]

In this paper, we report the synthesis, isolation, and X-ray crystallographic study of the first multi-CF_3 derivative of $Sc_3N@D_{5h}$-C_{80}, $Sc_3N@D_{5h}$-$C_{80}(CF_3)_{18}$, and three new isomers of $Sc_3N@I_h$-$C_{80}(CF_3)_{14}$, addressing systematically the interplay of the CF_3 addition patterns with cage distortions and the position of the encaged Sc_3N cluster.

EXPERIMENTAL SECTION

$Sc_3N@D_{5h}$-C_{80} and $Sc_3N@I_h$-C_{80} were synthesized using a modified Krätschmer-Huffman DC-arc discharging method according to a

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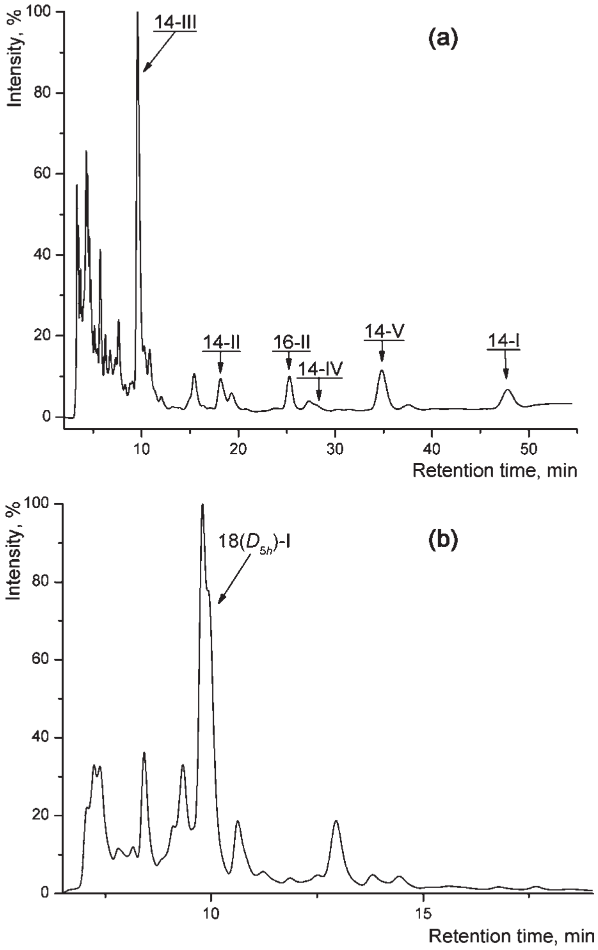

Figure 1. HPLC traces of $Sc_3N@I_h$-$C_{80}(CF_3)_n$ (a) and $Sc_3N@D_{5h}$-$C_{80}(CF_3)_n$ (b) in hexane. The fractions containing isomers of known structures are shown by arrows. Abbreviations indicate the number of CF_3 groups (14 or 16) and the consecutive number of the isomer (Roman numerals; see text for numbering details). Isomer **14-II** was identified on the basis of the previous work.[7]

previously reported procedure with the addition of N_2 (10 mbar) into 400 mbar of He, using a mixture of Sc_2O_3 (99.99%) and graphite powder (molar ratio of Sc/C = 1:15).[8] The as-produced soot was Soxhlet-extracted by CS_2 for 24 h. After removing CS_2, toluene was added immediately to redissolve the product. The solution was subsequently passed through a 0.2 μm Telflon filter for HPLC separation, which was achieved by recycling HPLC running on an LC-9104 HPLC (JAI, Japan) using a Cosmosil 5PYE column (20 mm i.d. × 250 mm, Nacalai Tesque Inc.) and toluene as the eluent at a flow rate of 15 mL min^{-1} (see the Supporting Information).

The synthesis of $Sc_3N@C_{80}(CF_3)_n$ was carried out using the method described for the trifluoromethylation of empty fullerenes.[9] $Sc_3N@D_{5h}$-C_{80} (ca. 1 mg) or $Sc_3N@I_h$-C_{80} (ca. 4 mg) was placed in a three-section glass ampule. An excess of CF_3I (ca. 0.5 mL) was condensed upon cooling with liquid nitrogen in the ampule, which was evacuated and sealed off. The section containing endohedral fullerene was heated at 400(±5) °C in an oven, whereas the section with CF_3I remained at room temperature, thus providing the pressure of 5−6 bar. About 90% of the starting $Sc_3N@C_{80}$ was trifluoromethylated after 48 h and deposited as a deep-orange sublimate in the less heated part of the ampule. The ampule was cooled to room temperature and then opened. The excess CF_3I was evaporated, and elemental iodine was removed by heating at ca. 100 °C in the open air for several hours.

The sublimate obtained in the experiments with $Sc_3N@C_{80}$ (D_{5h} or I_h) contained a mixture of $Sc_3N@C_{80}(CF_3)_n$ (n = 14, 16, 18), with the most abundant compounds being observed for n = 16 and 18 for $Sc_3N@D_{5h}$-$C_{80}(CF_3)_n$ and n = 14 and 16 for $Sc_3N@I_h$-$C_{80}(CF_3)_n$ according to negative-ion MALDI-TOF MS analysis (Bruker AutoFlex reflectron time-of-flight mass spectrometer, N_2 laser, *trans*-2-(3-(4-tert-Butyl-phenyl)-2-methyl-2-propenylidene)malononitrile (DCTB) matrix; matrix-to-analyte ratio of ca. 1000).

The mixture of $Sc_3N@C_{80}(CF_3)_n$ (I_h or D_{5h}) was dissolved in hexane and subjected to HPLC separation using a Cosmosil Buckyprep column (10 mm i.d. × 250 mm, Nacalai Tesque Inc.) and hexane as the eluent at a flow rate of 4.6 mL min^{-1}, monitored at 290 nm. In the HPLC separation of $Sc_3N@I_h$-$C_{80}(CF_3)_n$ (Figure 1), 38 fractions with retention times from 3.5 to 48 min were collected. The fraction with a retention time of 34.9 min was additionally separated by recycling HPLC at a flow rate of 2.3 mL min^{-1}. The fractions eluted at 9.6, 25.3, 28.4, 34.9 (after recycling), and 47.8 min (Figure 1a) gave small crystals after slow evaporation of hexane or recrystallization from toluene or *p*-xylene. For the case of $Sc_3N@D_{5h}$-$C_{80}(CF_3)_n$, only the chromatographic fraction eluted at ca. 10.0 min (shoulder in Figure 1b) gave small crystals after recrystallization from toluene.

Data collection for single crystals was carried out with a MAR225 CCD detector at 100 K using synchrotron radiation at the BESSY storage ring, BL 14.2 (λ = 0.9050 Å, PSF of the Free University of Berlin, Germany). The structures were solved using direct methods (SHELXS97) and anisotropically refined against $|F^2|$ with SHELXL97. Crystallographic data and some details of data collection and structure refinement are summarized in Table 1. The molecular structures of $Sc_3N@I_h$-$C_{80}(CF_3)_{14}$-I (hexane solvate) and $Sc_3N@I_h$-$C_{80}(CF_3)_{16}$-II (xylene solvate) abbreviated as **14-I** and **16-II**, respectively (cage symmetry of I_h is omitted for brevity), were found to be the same to those reported previously.[6,7] The compound of **16-II** (1.06 *p*-xylene) contains two crystallographically independent **16-II** molecules. Note that this structure is determined with much lower accuracy than those of the toluene and hexane solvates of **16-II**.[7] Three other compounds with 14 CF_3 groups turned out to represent new isomers of $Sc_3N@I_h$-$C_{80}(CF_3)_{14}$ which are abbreviated as **14-III** (toluene solvate), **14-IV** (xylene solvate), and **14-V** (toluene solvate). In structure **14-V**, one of the three Sc atoms is disordered over three positions with occupancy factors of 0.72/0.15/0.13. Roman numbers III−V are used in the abbreviations of new isomers, because notations **14-I** and **14-II** have been already utilized for the compounds reported in refs 6 and 7.

An X-ray single-crystal diffraction study of the crystals chromatographically isolated from the $Sc_3N@D_{5h}$-$C_{80}(CF_3)_n$ mixture revealed the molecular structure of $Sc_3N@D_{5h}$-$C_{80}(CF_3)_{18}$ (Table 1). Hereafter, this isomer is abbreviated as **18(D_{5h})-I**. In spite of low accuracy due to low crystallinity, possibly resulting from a partial loss of the solvent, this molecule did not show any unusual distortions. Its addition pattern has been determined unambiguously.

RESULTS AND DISCUSSION

According to chromatographic data (Figure 1), high temperature trifluoromethylation of $Sc_3N@C_{80}$ with both I_h and D_{5h} isomers of $Sc_3N@C_{80}$ results in the products, $Sc_3N@C_{80}$-$(CF_3)_{14-18}$, with a relatively narrow range of compositions. However, the isomeric composition was found to be rather rich, thus evidencing a rather kinetic control of the reactions. It is noteworthy that a high temperature reaction of $Sc_3N@I_h$-C_{80} with silver trifluoroacetate performed in a sealed tube typically produces $Sc_3N@I_h$-$C_{80}(CF_3)_n$ with a very wide range of compositions with n from 2 to 18.[6] In the second round of trifluoromethylation of $Sc_3N@I_h$-$C_{80}(CF_3)_n$ with a much higher excess of $Ag(CF_3CO_2)$, the compounds with n ranging from 12

Table 1. Crystallographic Data and Some Details of Data Collection and Refinement for Six Crystal Structures of $Sc_3N@C_{80}(CF_3)_n$

compound	14-I	14-III	14-IV	14-V	16-II	18(D_{5h})-I
solvent in the lattice	0.5 hexane	toluene	1.06 *p*-xylene	toluene	1.06 *p*-xylene	0.75 toluene
fw	2118.92	2167.96	2188.63	2167.96	2326.65	2420.70
cryst syst	monoclinic	triclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (Å)	15.8238(5)	13.313(1)	13.5691(6)	13.0904(4)	30.718(3)	13.562(1)
b (Å)	19.5410(6)	14.278(1)	15.4401(6)	26.1495(7)	15.019(1)	14.634(1)
c (Å)	21.2054(6)	20.957(1)	18.5318(9)	19.8840(8)	38.040(4)	21.672(1)
α (deg)	90	80.60(1)	73.400(8)	90	90	86.53(1)
β (deg)	94.252(1)	80.86(1)	71.428(8)	96.226(1)	92.84(1)	72.12(1)
γ (deg)	90	62.61(1)	72.044(9)	90	90	76.20(1)
volume ($Å^3$)	6538.9(3)	3473.5(4)	3424.6(3)	6766.3(4)	17528(8)	3974.9(4)
Z	4	2	2	4	8	2
D_c/g cm^{-3}; μ /mm^{-1}	2.152; 0.983	2.073; 0.887	2.122; 0.902	2.128; 0.911	2.856; 1.183	2.023; 0.837
temp (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
reflns collected/R_{int}	72895/0.056	44210/0.024	41016/0.068	93167/0.054	111806/0.08	23499/0.113
data/params	13635/1476	12148/1435	11299/1333	14635/1409	23729/2734	8595/1020
R_1 [$I \geq 2\sigma(I)$]/wR_2 all)[a]	0.058/0.143	0.058/0.140	0.088/0.232	0.068/0.183	0.179/0.403	0.193/0.474
$\Delta\rho$ (max/min; e $Å^{-3}$)	1.11/−0.85	0.72/−0.40	0.92/−0.64	0.99/−0.52	1.00/−0.80	1.06/−0.74

[a] Definitions: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma\, w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

Table 2. Selected Distances (Å) and Angles (deg) of Sc_3N Moieties in the $Sc_3N@D_{5h}$-$C_{80}CF_3)_{18}$ and $Sc_3N@I_h$-$C_{80}CF_3)_{14}$ Molecules[a]

distance/angle[b]	14-I[c]	14-II[7]	14-III	14-IV	14-V	18-I (D_{5h})
Sc1−N	2.044(2)	1.996(4)	2.028(3)	2.023(6)	2.019(3)	2.01(2)
Sc2−N	2.037(2)	2.032(5)	2.013(3)	2.042(6)	2.057(4)	1.98(2)
Sc3−N	1.991(2)	2.015(5)	2.011(3)	1.991(6)	1.993(3)	2.03(2)
Sc1−N−Sc2	137.0(1)	138.0(3)	135.2(1)	135.2(3)	134.6(2)	129(1)
Sc1−N−Sc3	120.1(1)	106.5(2)	116.2(1)	119.4(3)	122.6(2)	122(1)
Sc2−N−Sc3	102.9(1)	114.2(2)	108.2(1)	105.4(3)	102.5(2)	109(1)
Sc1−C	2.274(3)	2.272(5)	2.260(3)	2.262(7)	2.291(4)	2.31(3)
Sc1−C	2.311(3)	2.282(5)	2.312(3)	2.310(7)	2.300(3)	2.38(3)
Sc2−C	2.229(3)	2.260(5)	2.275(3)	2.260(7)	2.208(5)	2.22(3)
Sc2−C	2.302(3)	2.320(5)	2.284(3)	2.260(7)	2.289(5)	2.28(3)
Sc3−C	2.242(3)	2.231(6)	2.219(3)	2.246(8)	2.200(4)	2.31(3)
Sc3−C	2.289(3)	2.302(6)	2.316(3)	2.285(8)	2.284(3)	2.33(3)

[a] Data for structure **16-II** (xylene solvate) are not given here because this molecule was discussed in ref 7 on the basis of a more accurately determined crystal structure. [b] Only the two shortest Sc−C distances are selected. [c] Similar data are found in refs 6 and 7.

to 20 have been produced. Therefore, our ampule method of reacting $Sc_3N@C_{80}$ with CF_3I at high pressure possesses a higher selectivity in respect to composition (n = 14−18).

Some common structural features of multi-CF_3 derivatives of $Sc_3N@I_h$-C_{80} such as rigid fixation of both the I_h-C_{80} cage and the Sc_3N cluster, strong angular distortions of the latter were revealed previously for two isomers of $Sc_3N@I_h$-$C_{80}(CF_3)_{14}$ (**14-I** and **14-II**) and two isomers of $Sc_3N@I_h$-$C_{80}(CF_3)_{16}$ (**16-I** and **16-II**) as well as for single isomers of mutually related $Sc_3N@I_h$-$C_{80}(CF_3)_{10}$ and $Sc_3N@I_h$-$C_{80}(CF_3)_{12}$.[6,7] In the present work, due to a more elaborate HPLC separation, such as lower flow rates or the use of recycling chromatography, additional isomers of $Sc_3N@I_h$-$C_{80}(CF_3)_{14}$ (**14-III** to **14-V**) have been isolated. Their structural characterization was made possible due to additional efforts on recrystallization from different solvents. Therefore, it is appropriate to compare all five isomers with a known structure in more detail. Selected geometric parameters of five $Sc_3N@I_h$-$C_{80}(CF_3)_{14}$ isomers are given in Table 2, and their Schlegel diagrams are presented in Figure 2.

Common features of all isomers **14-I**−**14-V** are nearly perfect planarity of the Sc_3N units, ordered positions of the I_h-C_{80} cage and Sc_3N unit (except for **14-V**), attachment of CF_3 groups in positions of both PHJs (pentagon-hexagon-hexagon junctions) and THJs (triple hexagon junctions), and the η^2-like coordination of all endohedral Sc atoms to the I_h-C_{80} cage. In fact, the coordination of Sc atoms via d−π interaction includes more than the two nearest carbon atoms of the fullerene cage; a certain ionic contribution should also be present due to electron donation from Sc to the cage.[10] However, in all isomers, two Sc−C distances, 2.22−2.32 Å, are shorter than others, thus roughly

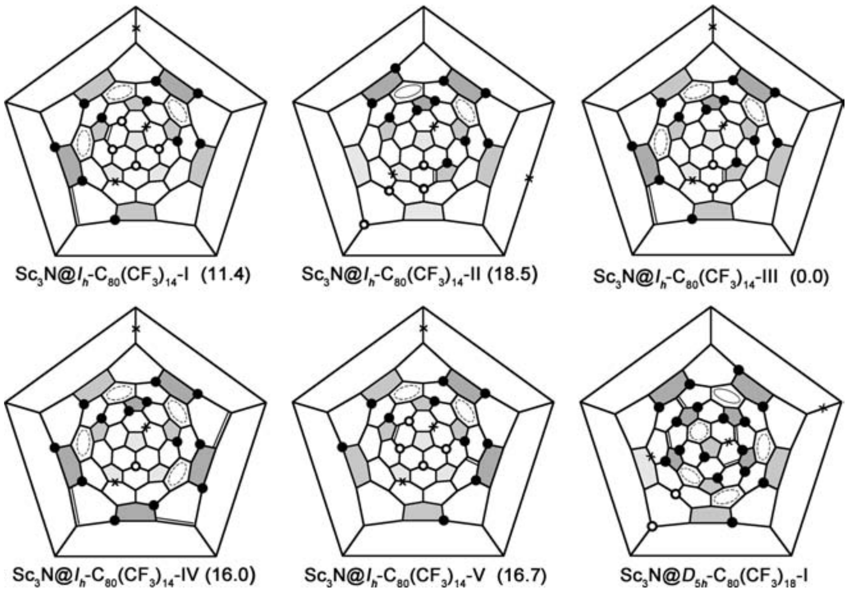

Figure 2. Schlegel diagrams of $Sc_3N@D_{5h}$-$C_{80}(CF_3)_{18}$ (**18**(D_{5h})**-I**) and the five $Sc_3N@I_h$-$C_{80}(CF_3)_{14}$ isomers (**14-I**−**14-V**). Black and empty circles indicate the cage carbons at PHJ and THJ positions, respectively, bearing CF_3 groups. Crosses denote the C−C bonds with C atoms closest to Sc atoms. Pentagons with two, one, and no attached CF_3 groups are highlighted with dark, medium, and light gray, respectively, with exceptions for the outer pentagons. Nearly double C−C bonds and aromatic rings are also indicated. Relative formation energies (kJ mol^{-1}) of **14-I**−**14-V** isomers are given in the parentheses.

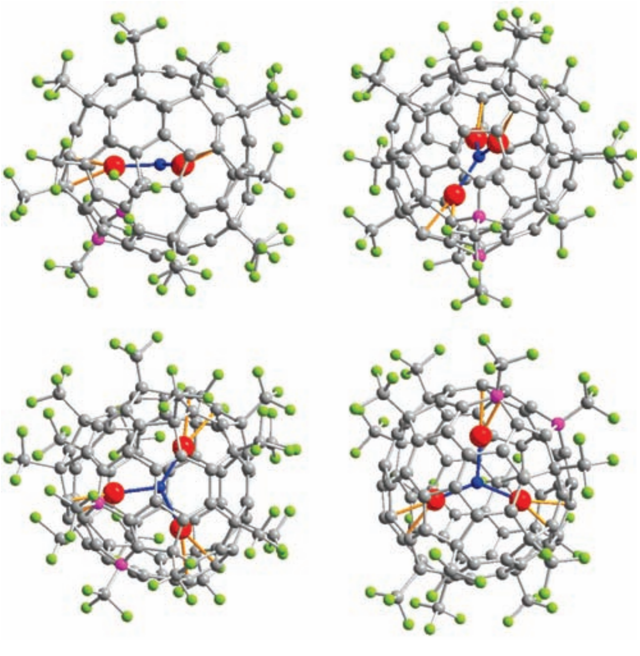

Figure 3. Two projections of $Sc_3N@D_{5h}$-$C_{80}(CF_3)_{18}$ (**18**(D_{5h})**-I**, left) and $Sc_3N@I_h$-$C_{80}(CF_3)_{14}$ (**14-III**, right). Sc, red; N, blue; C, gray and violet (for sp^3 THJ); F, green; Sc−C bonds, orange. Top projections are given in the same orientation as the corresponding Schlegel diagrams in Figure 2. Bottom projections are given perpendicular to Sc_3N planes.

resembling the η^2 coordination (see Table 2). In all structures, Sc−N distances are in a narrow range of 1.99−2.06 Å, whereas Sc_3N arrangements strongly deviate from trigonal symmetry with Sc−N−Sc angles lying in a wide range from 102° to 138°. Addition to C atoms in the position of THJ is considered to be energetically unfavorable in the case of empty fullerenes.[11] However, it seems to be less unfavorable for endohedral fullerenes. The number of sp^3 THJs varies from one (**14-IV**) and two (**14-III**; see Figure 3) to four (**14-I, 14-II,** and **14-V**). It is noteworthy that the number of sp^3 THJs in two known $Sc_3N@C_{80}(CF_3)_{16}$ isomers is four and even eight in structures of **16-II** and **16-I**, respectively.[6,7] It should be noted that, very recently, one more isomer with 14 CF_3 groups was isolated from the products of the synthesis with $Ag(CF_3CO_2)$.[6b] Its possible addition pattern suggested on the basis of ^{19}F NMR and supported by theoretical calculations contains a single ribbon of edge-sharing $C_6(CF_3)_2$ hexagons and $C_5(CF_3)_2$ pentagons, including one CF_3 group attached at THJ. Apparently, its structure is substantially different from that our **14-IV**, in the structure of which the CF_3 group at THJ is isolated.

In structures **14-I**−**14-V**, CF_3 groups are not distributed uniformly on fullerene cages. Among the 12 pentagons of the I_h-C_{80} cage, several have two attached groups in 1,3 positions. Others have only one CF_3 group, whereas the remaining have no exohedral attachment at all. The attachment of CF_3 groups results in the formation of fully or partially isolated double C−C bonds (C−C, 1.33−1.37 Å) and aromatic (benzenoid) cycles (averaged C−C, 1.39−1.40 Å), as indicated on the Schlegel diagrams. Notably, carbon atoms of isolated or semi-isolated benzenoid rings and double bonds appear to not participate in coordination of the Sc atoms. Instead, areas on the fullerene cage on or near "empty" pentagons are suitable for endohedral coordination to scandium, probably due to their acceptor capacities.

A closer inspection of the Schlegel diagrams allows a more detailed comparison of addition patterns of the five $Sc_3N@I_h$-$C_{80}(CF_3)_{14}$ isomers. All isomers have quite similar arrangements of CF_3 groups so that many of 14 attachment positions are the same. Thus, isomer **14-I** possesses 8, 11, 11, and 12 common attachment positions with isomers **14-II, 14-III, 14-IV**, and **14-V**, respectively. At the same time, isomer **14-III** has 11, 12, and 9 common positions of CF_3 groups with isomers **14-II**, **14-IV**, and **14-V**, respectively. Significantly, the position of the Sc_3N cluster is the same in isomers **14-I** and **14-III**−**14-V**, whereas its orientation is different in **14-II** due to the changes in the coordination of two Sc atoms (see the crosses on the Schlegel diagrams in Figure 2) accompanied by the change in the distortion of the Sc_3N cluster (see Sc−N−Sc angles in Table 2) and the orientation of the Sc_3N plane by ca. 30°. This reorientation occurs due to the change in the attachment positions of two CF_3 groups in **14-II**, thus preventing coordination of Sc atoms in the nearest area of the I_h-C_{80} cage. A further distinguishing feature of isomer **14-II** is that one 6:6 and two 5:6 C−C bonds of the cage are coordinated by Sc atoms, whereas the situation is reversed in all other isomers (Figure 2). It turns out that the exohedral attachment directly influences the endohedral one, i.e., the position of the Sc_3N cluster inside the I_h-C_{80} cage. One of the conclusions in ref 6a was formulated as a mutual influence of the CF_3 addition pattern and the position of the Sc_3N cluster on the whole structure. However, in the subsequent investigation,[6b] the same authors consider the addition pattern as a more important factor, because in their methodology in computational searching for the most stable $Sc_3N@I_h$-$C_{80}(CF_3)_n$ isomers, they vary the position of the Sc_3N moiety only after the optimal $(CF_3)_n$ addition pattern has been chosen.

Our DFT calculations of relative formation energies of isomers **14-I**−**14-V** revealed the somewhat higher stability of isomer **14-III** (0.0 kJ mol^{-1}), whereas isomer **14-II** has the lowest stability (18.5 kJ mol^{-1}; see Figure 2). Obviously, these differences cannot be simply attributed to the number of sp^3 THJs, double bonds, and benzenoid rings on the C_{80} fullerene cage or to the position of the Sc_3N cluster inside the cage. However, it is worth noting that the most stable isomer, **14-III**, has only three "empty" (unoccupied with CF_3 groups) pentagons, which are located near (or include) the C−C bonds coordinated by Sc atoms and may serve as negative charge acceptors. All other $Sc_3N@I_h$-$C_{80}(CF_3)_{14}$ isomers have additionally one or two empty pentagons that possibly destabilize the whole molecule.

For **18**(D_{5h})**-I** as the first multi-CF_3 derivative of $Sc_3N@D_{5h}$-C_{80}, its structure has some common features with $Sc_3N@I_h$-$C_{80}(CF_3)_{14}$ such as the presence of "empty" pentagons (only two), sp^3 THJs (two), and isolated C−C double bonds and benzenoid rings (see Figure 2). Due to the addition of a larger number of CF_3 groups, the numbers of (semi)isolated double bonds (4) and aromatic rings (5) are also larger in **18**(D_{5h})**-I** compared to all $Sc_3N@I_h$-$C_{80}(CF_3)_{14}$ isomers. Interestingly, in **18**(D_{5h})**-I**, the Sc_3N cluster possesses smaller angular deviations from trigonal symmetry (Sc−N−Sc angles 110−129° instead of 120°) than those in the pristine $Sc_3N@D_{5h}$-C_{80} (107−132°).[3] An additional difference concerns the coordination of the Sc atoms to one 5:6 C−C and two 6:6 C−C bonds in **18**(D_{5h})**-I**, whereas a reversed situation is observed in the nonfunctionalized molecule. Moreover, the position of the Sc_3N plane nearly parallel to the (former) D_5 axis (see Figure 3) is fully different from that in the pristine $Sc_3N@D_{5h}$-C_{80} molecule (at 60°).[3] In **18**(D_{5h})**-I**, more C atoms, such as bearing CF_3 groups or belonging to benzenoid rings and isolated double bonds, are excluded for coordination by Sc. There are only two "empty" cage pentagons, and both are utilized for coordination to scandium, whereas the third Sc atom (Sc1) coordinates a C−C bond in a lesser delocalized area of the carbon cage (see Figure 2). Notably, a Sc1−C distance of 2.38(3) Å, the longest one among all Sc−C distances selected in Table 2 for six $Sc_3N@C_{80}(CF_3)_n$ molecules, corresponds to the coordination of a Sc atom to a C atom involved in the semi-isolated C−C double bond. Therefore, like in structures of **14-I**−**14-V**, in **18**(D_{5h})**-I**, the addition pattern of CF_3 groups has a directing effect on the position of the Sc_3N unit inside the D_{5h}-C_{80} cage.

■ CONCLUSIONS

In summary, we have successfully synthesized and isolated the first multi-CF_3 derivative of $Sc_3N@D_{5h}$-C_{80}, $Sc_3N@D_{5h}$-$C_{80}(CF_3)_{18}$, and three new isomers of $Sc_3N@I_h$-$C_{80}(CF_3)_{14}$ (**14-III**−**14-V**). An X-ray crystallographic study revealed that, in all cases, the addition pattern of CF_3 groups governs the position of the Sc_3N unit inside the fullerene D_{5h}-C_{80} or I_h-C_{80} cage. The interplay of the CF_3 addition patterns with cage distortions and the position of the encaged Sc_3N cluster revealed in this study provides deeper insight into the structural chemistry of trifluoromethylated derivatives of endohedral fullerenes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Isolation of $Sc_3N@D_{5h}$-C_{80} and $Sc_3N@I_h$-C_{80}, DFT calculation details, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) For recent reviews, see: (a) Dunsch, L.; Yang, S. F. *Small* **2007**, *3*, 1298–1320. (b) Dunsch, L.; Yang, S. F. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3067–3081.

(2) (a) Stevenson, S.; Rice, G.; Glass, T.; Harich, K.; Cromer, F.; Jordan, M. R.; Craft, J.; Hadju, E.; Bible, R.; Olmstead, M. M.; Maitra, K.; Fisher, A. J.; Balch, A. L.; Dorn, H. C. *Nature* **1999**, *401*, 55. (b) Stevenson, S.; Fowler, P. W.; Heine, T.; Duchamp, J. C.; Rice, G.; Glass, T.; Harich, K.; Hajdu, E.; Bible, R.; Dorn, H. C. *Nature* **2000**, *408*, 427. (c) Stevenson, S.; Lee, H. M.; Olmstead, M. M.; Kozikowski, C.; Stevenson, P.; Balch, A. L. *Chem.—Eur. J.* **2002**, *8*, 4528. (d) Yang, S. F.; Troyanov, S. I.; Popov, A. A.; Krause, M.; Dunsch, L. *J. Am. Chem. Soc.* **2006**, *128*, 16733. (d) Stevenson, S.; Chancellor, C. J.; Lee, H. M.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **2008**, *47*, 1420.

(3) Cai, T.; Xu, L.; Anderson, M. R.; Ge, Z.; Zuo, T.; Wang, X.; Olmstead, M. M.; Balch, A. L.; Gibson, H. W.; Dorn, H. C. *J. Am. Chem. Soc.* **2006**, *128*, 8581.

(4) Chaur, M. N.; Melin, F.; Ortiz, A. L.; Echegoyen, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 7514 and references therein.

(5) Shustova, N. B.; Popov, A. A.; Mackey, M. A.; Coumbe, C. E.; Phillips, J. P.; Stevenson, S.; Strauss, S. H.; Boltalina, O. V. *J. Am. Chem. Soc.* **2007**, *129*, 11676.

(6) (a) Shustova, N. B.; Chen, Y.-S.; Mackey, M. A.; Coumbe, C. E.; Phillips, J. P.; Stevenson, S.; Popov, A. A.; Boltalina, O. V.; Strauss, S. H. *J. Am. Chem. Soc.* **2009**, *131*, 17630.(b) Shustova, N. B.; Peryshkov, D. V.; Kyvychko I. V.; Chen, Y.-S.; Mackey, M. A.; Coumbe, C. E.; Heaps. D. T.; Confait B. S.; Heine T.; Phillips, J. P.; Stevenson, S.; Dunsch L.; Popov, A. A.; Strauss, S. H.; Boltalina, O. V. *J. Am. Chem. Soc.* **2011**, *133*, 2672.

(7) Yang, S. F.; Chen, C. B.; Lanskikh, M. A.; Tamm, N. B.; Kemnitz, E.; Troyanov, S. I. *Chem. Asian J.* **2011**, *6*, 505.

(8) Yang, S. F.; Chen, C.; Popov, A. A.; Zhang, W. F.; Liu, F. P.; Dunsch, L. *Chem. Commun.* **2009**, 6391.

(9) Ignat'eva, D. V.; Goruynkov, A. A.; Tamm, N. B.; Ioffe, I. N.; Avdoshenko, S. M.; Sidorov, L. N.; Dimitrov, A.; Kemnitz, E.; Troyanov, S. I. *Chem. Commun.* **2006**, 1778.

(10) Alvarez, L.; Pichler, T.; Georgi, P.; Schwieger, T.; Peisert, H.; Dunsch, L.; Hu, Z.; Knupfer, M; Fink, J.; Bressler, P.; Mast, M.; Golden, M. S. *Phys. Rev. B* **2002**, *66*, 035107.

(11) Simeonov, K. S.; Amsharov, K. Yu.; Jansen, M. *Chem.—Eur. J.* **2009**, *15*, 1812.