Communication

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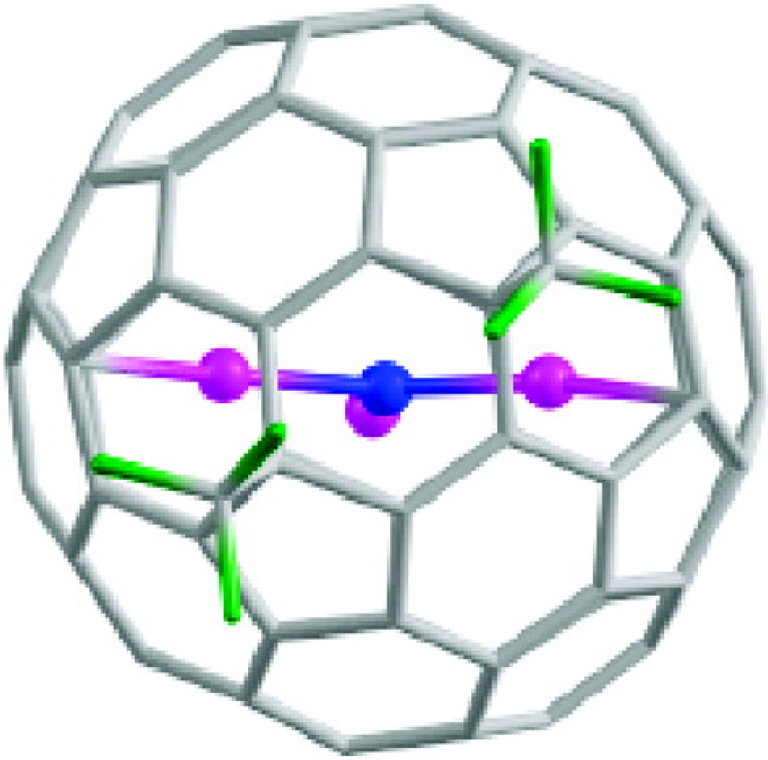
J. Am. Chem. Soc., **2007**, 129 (38), 11676-11677• DOI: 10.1021/ja074332g • Publication Date (Web): 01 September 2007



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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COMMUNICATIONS

Radical Trifluoromethylation of $Sc_3N@C_{80}$

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Endohedral metallic nitride fullerenes (MNFs; a subset of endohedral metallofullerenes, EMFs) have attracted increasing attention since their discovery,[1] not only because they possess unique structures but also because exohedral derivatives of them may find use in important medical applications such as MRI or X-ray contrast agents.[2] Recently, some of us developed an efficient, nonchromatographic purification that makes these compounds available in larger quantities than any EMF reported to date.[3] Exohedral modifications of MNFs have been largely limited to cycloadditions.[4] Taken together, refs 3, 4 and references therein have repeatedly shown that the $Sc_3N@(C_{80}\text{-}I_h)$ isomer is *much* less reactive than the D_{5h} cage isomer.

We now report the preparation, isolation, and spectroscopic and electrochemical characterization of the first CF_3 derivatives of both isomers of $Sc_3N@C_{80}$.[5] Hollow fullerene$(CF_3)_n$ derivatives are sufficiently volatile to sublime out of the hot zone during reaction with flowing CF_3I;[6] EMF$(CF_3)_n$ compounds are not,[7] and the compounds described here were extracted from the crude product mixture with organic solvents. The first washings (hexane and toluene) contained $Sc_3N@C_{80}(CF_3)_n$ ($8 \le n \le 12$; these will be described in the full paper). The *o*-dichlorobenzene washings contained predominantly two compositions, $Sc_3N@C_{80}$ and $Sc_3N@C_{80}(CF_3)_2$, (5:1 HPLC peak areas ratio), with small amounts of $Sc_3N@C_{80}(CF_3)_{4,6}$. Mass and ^{19}F NMR spectra of HPLC-purified $Sc_3N@C_{80}(CF_3)_2$[8] are shown in Figure 1. The *bis*-CF_3 derivative prepared with purified $Sc_3N@C_{80}\text{-}I_h$ exhibited an ^{19}F singlet at δ −71.4, indicating either symmetry-related CF_3 groups or CF_3 groups rendered chemical-shift equivalent by rapid reorientation of the Sc_3N cluster inside the cage. The derivative prepared with the 9:1 mixture of cage isomers exhibited two singlets, at δ −71.4 (rel. int. 7) and −73.3 (rel. int. 1). It is virtually certain that the compound with δ −73.3 belongs to $Sc_3N@(C_{80}\text{-}D_{5h})$. Therefore, notwithstanding the previously reported differences in reactivity of $Sc_3N@(C_{80}\text{-}I_h)$ and $Sc_3N@(C_{80}\text{-}D_{5h})$, we conclude that these two compounds react with CF_3 radicals at essentially the same rate at 520 ± 10 °C.

If we avoid triple-hexagon junctions and assume para addition of two CF_3 groups to a $C_{80}\text{-}I_h$ hexagon, which is the most likely addition pattern,[9] there are still many possible orientations of the Sc_3N cluster. DFT calculations (see ref 6 for details) were performed for more than 20 isomers of $Sc_3N@(C_{80}\text{-}I_h)(CF_3)_2$ in which different cluster positions were chosen as starting points for geometry optimization. The two most stable optimized structures each have two of the three Sc atoms bonded to the cage C atom that is para to each of the cage $C(CF_3)$ atoms, as shown in Figure 2. This results in a para[3] ribbon of edge sharing hexagons with the sequence $C(Sc)\cdots C(CF_3)\cdots C(CF_3)\cdots C(Sc)$. Para only sequences of $C_6(CF_3)_2$ hexagons have been reported for $C_{70}Y_8$,[10] $C_{74}Y_{12}$,[6b] and $C_{78}Y_{12}$[6b] ($Y = CF_3$, all studied by X-ray diffraction). Metal atoms bonded to sp^2 cage C atoms that are para to sp^3 cage C atoms have been observed in cycloadducts of $Y_3N@(C_{80}\text{-}I_h)$[11] and $Sc_3N@(C_{80}\text{-}I_h)$.[4a,12] The two lowest energy isomers differ only in the position of the third Sc atom, and the DFT-calculated energy difference between them is less than 2 kJ mol^{-1}. Both isomers are slightly distorted from ideal C_2 symmetry in that the Sc atom farthest from the CF_3

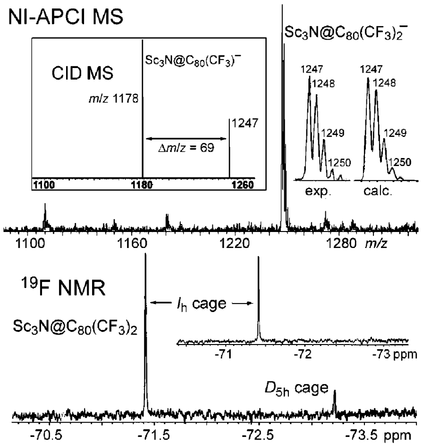

Figure 1. Top: Negative-ion APCI mass spectrum of $Sc_3N@C_{80}(CF_3)_2$. The left inset is the CID mass spectrum of the *m/z* 1247 molecular ion, in which the dominant fragment is due to CF_3 loss. The right inset shows the calculated and observed isotope distributions. Bottom: ^{19}F NMR spectrum of a mixture of $Sc_3N@(C_{80}\text{-}I_h)(CF_3)_2$ and $Sc_3N@(C_{80}\text{-}D_{5h})(CF_3)_2$ ($CDCl_3$, 376.5 MHz, C_6F_6 internal standard, (δ −164.9)). The inset is the ^{19}F NMR spectrum of pure $Sc_3N@(C_{80}\text{-}I_h)(CF_3)_2$.

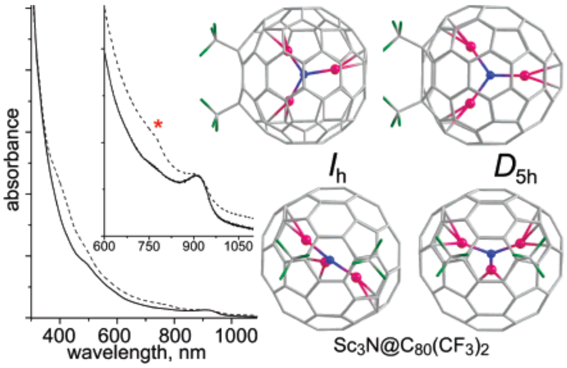

Figure 2. UV−vis−NIR spectra (toluene) of $Sc_3N@(C_{80}\text{-}I_h)(CF_3)_2$ (solid line) and a mixture of $Sc_3N@(C_{80}\text{-}I_h)(CF_3)_2$ and $Sc_3N@(C_{80}\text{-}D_{5h})(CF_3)_2$ (dashed line). The inset shows an expansion of part of the spectrum. The asterisk denotes the band assigned to the lowest energy transition in $Sc_3N@(C_{80}\text{-}D_{5h})(CF_3)_2$. Also shown are the most-stable DFT optimized isomers of $Sc_3N@(C_{80}\text{-}I_h)(CF_3)_2$ and $Sc_3N@(C_{80}\text{-}D_{5h})(CF_3)_2$.

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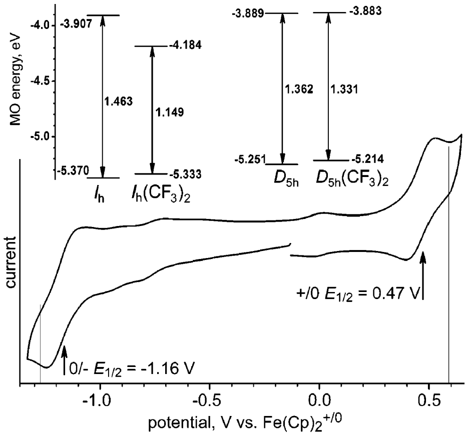

Figure 3. Top: DFT HOMO and LUMO energies of I_h and D_{5h} isomers of $Sc_3N@C_{80}$ and $Sc_3N@C_{80}(CF_3)_2$. The arrows depict HOMO−LUMO gaps. Bottom: Cyclic voltammogram of $Sc_3N@(C_{80}\text{-}I_h)(CF_3)_2$ (0.1 M $TBABF_4$, *o*-dichlorobenzene, 25 °C, scan rate of 20 mV s^{-1}). Arrows show reduction (0/−) ($E_c = -1.24$ V, $E_a = -1.08$ V) and oxidation (+/0) $E_{1/2}$ ($E_a = 0.54$ V, $E_c = 0.40$ V) values. The vertical lines depict the 0/− and +/0 $E_{1/2}$ values for $Sc_3N@(C_{80}\text{-}I_h)$ measured under the same conditions.

groups is displaced from the center of its closest hexagon toward one of the $^5/_6$ junctions. Thus, on the NMR time scale, this Sc atom would undergo rapid reorientation with respect to the C atoms of its hexagon, resulting in apparent molecular C_2 symmetry and chemical-shift equivalent CF_3 groups.

Other DFT-optimized structures in which only one Sc atom is bonded to a cage C atom para to a CF_3 group are 13−21 kJ mol^{-1} less stable than the first two; all other isomers are 26−65 kJ mol^{-1} higher in energy. These results reveal a significant difference between $Sc_3N@(C_{80}\text{-}I_h)(CF_3)_2$ and $Sc_3N@(C_{80}\text{-}I_h)$. Variable-temperature ^{45}Sc NMR spectroscopy and DFT calculations have shown that the Sc_3N cluster effectively undergoes free rotation in $Sc_3N@(C_{80}\text{-}I_h)$.[1,13] Therefore, either 1,2 additions (i.e., cycloadditions to a cage C−C bond) or 1,4 additions (i.e., para addition of CF_3 groups to a hexagon) can substantially affect the dynamics of the cluster.

There is only one way to add two CF_3 groups to para positions of a $Sc_3N@(C_{80}\text{-}D_{5h})$ hexagon so that the CF_3 groups are symmetry related. By analogy to the DFT results for the I_h cage isomer, we suggest that two of the three Sc atoms are coordinated to cage carbon atoms that are para to the sp^3 $C(CF_3)$ atoms in $Sc_3N@(C_{80}\text{-}D_{5h})(CF_3)_2$, as shown in Figure 2. Figure 2 also shows the UV−vis−NIR absorption spectra of pure $Sc_3N@(C_{80}\text{-}I_h)(CF_3)_2$ and the mixture of $Sc_3N@(C_{80}\text{-}I_h)(CF_3)_2$ and $Sc_3N@(C_{80}\text{-}D_{5h})(CF_3)_2$. The lowest-energy transition of $Sc_3N@(C_{80}\text{-}I_h)(CF_3)_2$ occurs at 920 nm (1.35 eV), a significantly longer wavelength than the 735 nm (1.69 eV) value for the parent $Sc_3N@(C_{80}\text{-}I_h)$.[14] A shoulder at 772 nm (1.62 eV) is assigned to the lowest-energy transition of $Sc_3N@(C_{80}\text{-}D_{5h})(CF_3)_2$, which almost coincides with the 780 nm (1.59 eV) value for the parent $Sc_3N@(C_{80}\text{-}D_{5h})$.[14] Therefore, the addition of two CF_3 groups results in a 0.34 eV decrease in the $Sc_3N@(C_{80}\text{-}I_h)$ optical gap and a small increase of 0.03 eV in the $Sc_3N@(C_{80}\text{-}D_{5h})$ optical gap. The spectroscopic results support our structural assignments because they match the DFT-predicted frontier orbital energies, as shown in Figure 3.

$Sc_3N@(C_{80}\text{-}I_h)(CF_3)_2$ exhibited both a quasi-reversible reduction ($E_{1/2} = -1.16$ V vs $Fc(Cp)_2^{+/0}$) and oxidation ($E_{1/2} = 0.47$ V), as also shown in Figure 3. For comparison, the $E_{1/2}$ values for reduction and oxidation of parent $Sc_3N@(C_{80}\text{-}I_h)$ measured under the same conditions are −1.26 and 0.59 V, respectively (these are similar to the literature values[14,15]). The 0.22 V decrease in $\Delta E_{1/2}$ for the transformation $Sc_3N@(C_{80}\text{-}I_h) \rightarrow Sc_3N@(C_{80}\text{-}I_h)(CF_3)_2$ is in rough agreement with the 0.34 eV optical-gap decrease that occurs when two CF_3 groups are added.

Our results demonstrate for the first time that the MNFs $Sc_3N@(C_{80}\text{-}I_h)$ and $Sc_3N@(C_{80}\text{-}D_{5h})$ can be readily transformed into fluoroalkylated derivatives by using high-temperature R_f radical addition methodologies previously developed for fullerenes.[6,7] With the recent breakthrough in the large-scale production/purification of MNFs by nonchromatographic methods, it should be possible to prepare and utilize a new family of thermally stable, highly soluble materials with tunable electron-accepting properties.

Acknowledgment. We thank CRDF (Grant RUC2−2830-MO-06), NSF (Grants CHE-0547988 and DBI-0619455), and DOE (Grant P200A060323) for support.

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JA074332G