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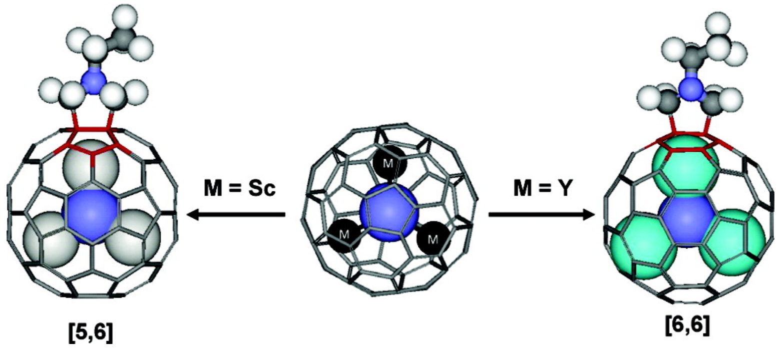

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Trimetallic Nitride Endohedral Metallofullerenes: Reactivity Dictated by the Encapsulated Metal Cluster

Claudia M. Cardona, Alex Kitaygorodskiy, and Luis Echegoyen*

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Abstract: The first derivatives of $Y_3N@C_{80}$ have been synthesized and fully characterized. 1,3-Dipolar cycloaddition of *N*-ethylazomethine ylide yielded mainly the pyrrolidine monoadduct of the icosahedral (I_h) symmetry cage exclusively at a [6,6] double bond. The same regioselectivity on a [6,6] double bond was observed when the endohedral compound was cyclopropanated with diethyl bromomalonate. These results are in pronounced contrast to those observed for icosahedral symmetry $Sc_3N@C_{80}$, for which all reported derivatives add completely regioselectively to [5,6] double bonds. ^{1}H NMR, ^{13}C NMR, and HMQC spectroscopy revealed that the addition pattern on $Y_3N@C_{80}$ resulted in a pyrrolidinofullerene derivative with unsymmetric pyrrolidine carbons and symmetric geminal protons. The cyclopropanated monoadduct exhibited symmetric ethyl groups on the malonate, consistent with regioselective addition at a [6,6] double bond. Attempts to perform the same cyclopropanation reaction on (I_h) $Sc_3N@C_{80}$ failed to yield any identifiable products. These observations clearly indicate that the reactivity of trimetallic nitride endohedral metallofullerenes toward exohedral chemical functionalization is profoundly affected and effectively controlled by the nature of the endohedral metal cluster.

Introduction

Since the beginning of fullerene research and discovery, people envisioned the insertion of atoms and molecules into the carbon cages and wondered how these modifications would affect their chemical and physical properties.[1] Since then, endofullerenes containing metals, noble gases, or other atoms have been discovered.[2]

The study of fullerenes containing metals, endohedral metallofullerenes, is quickly becoming one of the most interesting research areas within the field of carbon-based compounds because they present some intriguing properties.[3] Many of them are stable under ambient conditions even though in some cases the empty cages or the encapsulated moieties have never been isolated independently; their electronic structures differ greatly when compared to those of the parent empty cages; and several species have been isolated encapsulating metals with magnetic or radioactive characteristics. Therefore, they are already being considered in the future development of biomedical and nanomaterial sciences.[4]

Over the past decade, the difficulty in preparing and isolating macroscopic quantities of endohedral metallofullerenes has restricted further investigation into their physical and chemical properties and has limited exohedral functionalization of the carbon cages. Derivatization of these fullerene species is crucial in the development of new materials with potential applications in future technologies, and in the investigation of the role that

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any modification of the cage plays in tuning their properties. Just recently, many efforts have been reported to isolate pure samples of endohedral metallofullerenes in larger quantities.[5] A breakthrough occurred in 1999 when Dorn and co-workers first reported the family of encapsulated trimetallic nitride clusters inside fullerenes.[6] Their trimetallic nitride template (TNT) method to produce endohedral metallofullerenes has afforded macroscopic quantities of materials such as $Sc_3N@C_{80}$, with yields that exceed those of the abundant empty-cage C_{84}. The latter is the third most abundant fullerene (next to C_{60} and C_{70}) produced under normal conditions.[7] Their TNT method, with subsequent modifications,[8] has resulted in the preparation of many other members of this interesting family of compounds.[9]

Isolation of $Sc_3N@C_{80}$ in macroscopic quantities has facilitated the study of its physical structure.[10] There are seven possible constitutional isomers of C_{80} satisfying the isolated pentagon rule (IPR), yet only the most stable empty cages with D_2 and D_{5d} symmetry have been isolated. In contrast, the two least stable empty isomers with I_h and D_{5h} symmetries are the ones that predominate overwhelmingly when they are filled with metallic nitride clusters. Macroscopic quantities of this material has also allowed the evaluation of its electronic properties, and this research suggests a formal transfer of six electrons from the Sc_3N moiety to the fullerene cage.[8,11] In fact, an experimental report using photoemission and X-ray absorption spectroscopy determined an effective transfer of 6.3 electrons,[11c] and molecular orbital calculations predict that the HOMO is essentially a fullerene-based orbital, while the Sc_3N fragment represents the LUMO of this endohedral metallofullerene.[11b] This electronic transfer from the encapsulated cluster to the fullerene cage is a common feature in endohedral metallofullerenes. A negative surface charge brings into question the reactivity of the carbon sphere and thus the feasibility of performing chemical derivatizations on endohedral metallofullerenes.

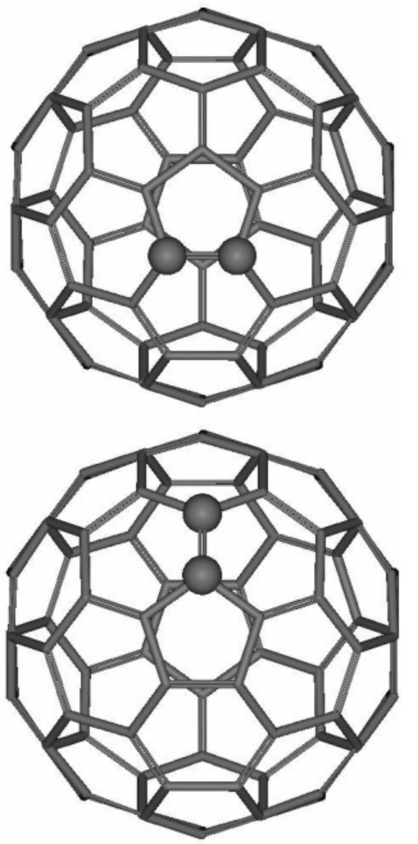

Figure 1. Two types of double bonds on I_h C_{80}: (Top) Double bond at a [5,6] ring junction abutted by two hexagons (a corannulene-type site). (Bottom) Double bond at a [6,6] ring junction abutted by a hexagon and a pentagon (a pyrene-type site).

However, since the first exohedral derivative of an endohedral metallofullerene was reported, $La@C_{82}(Mes_2Si)_2CH_2$,[12a] all results seem to indicate that metallofullerenes are very reactive toward organic functionalization, giving rise to multiple adducts or regioisomers of the monoadducts.[4a,12] Surprisingly, remarkable selectivity for specific regioisomeric monoadducts has been observed in three cases.[13] In one case, $La@C_{82}$ reacted photochemically with an adamantine-diazirine reagent to form a single isomer.[13a] The other two cases involved $Sc_3N@C_{80}$. The first derivative reported for this endohedral metallofullerene was a Diels−Alder monoadduct prepared by Dorn and co-workers,

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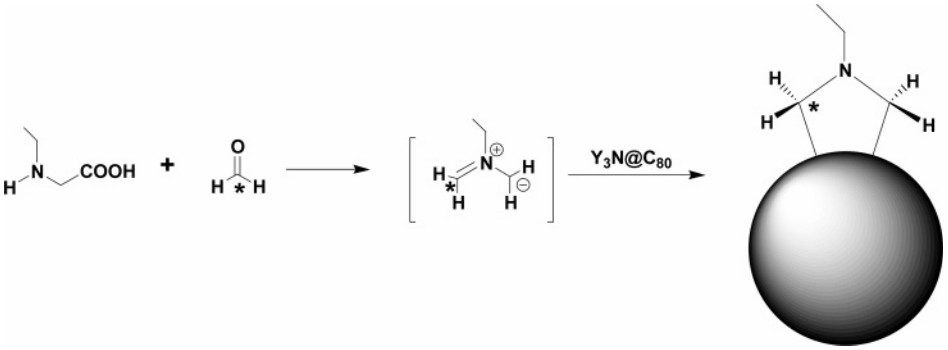
Scheme 1. Representation of the 1,3-Dipolar Cycloaddition of the ^{13}C-Enriched *N*-Ethyl Azomethine Ylide to $Y_3N@C_{80}$



which was characterized by NMR spectroscopy and X-ray crystallography as a single regioisomer.[13b,c] A more recent example was reported by us after 1,3-dipolar cycloaddition of an *N*-ethylazomethine ylide to the same compound, $Sc_3N@C_{80}$. An NMR study of this derivative showed that formation of the pyrrolidine ring occurs also regioselectively at the same [5,6] double bond as in the Diels−Alder case.[13d]

Here we report the first adduct derivatives of icosahedral $Y_3N@C_{80}$. One of these is obtained via 1,3-dipolar cycloaddition reaction of *N*-ethylazomethine ylide to yield mainly a pyrrolidine monoadduct.[14a] The other derivative is also a monoadduct, obtained via cyclopropanation with bromomalonate.[14b,c] Both of these cycloadditions occur regioselectively at a pyrene-type site, a double bond at a [6,6] ring junction abutted by a hexagon and a pentagon. These results are in marked contrast to addition at a corannulene-type site (a double bond at a [5,6] ring junction abutted by two hexagons), which is observed to occur regioselectively for both a Diels−Alder and a pyrrolidine adduct on $Sc_3N@C_{80}$ (Figure 1).[13b−d]

Results and Discussion

As of today, very little is known about the effect that the trimetallic nitride clusters have on the chemical and physical properties of endohedral metallofullerenes, and even less is known about the effect that this type of cluster has in the exohedral functionalization of such fullerenes. To the best of our knowledge, this is the first comparative study on the chemical reactivity of $M_3N@C_{80}$ upon changing the nature of the metal M (Sc, Y) in the endohedral metal nitride.

The groups of Nagase and Akasaka have investigated extensively the functionalization of endohedral metallofullerenes with disiliranes.[12a,c,d,15] They have shown the strong electron-accepting character of monometallofullerenes (La@C_{82}, Gd@C_{82}, Pr@C_{82}) and dimetallofullerenes ($La_2@C_{80}$, $Sc_2@C_{84}$) which facilitates their thermal addition to disiliranes. Such exohedral derivatizations also occur photochemically with these species. They have also shown that such functionalization only occurs photochemically with empty cages such as C_{60}, C_{70}, C_{76}, C_{78}, C_{82}, or C_{84}, which demonstrates that the reactivity depends on whether an endohedral metal species is present. However, there seems to be no difference in reactivity by varying the nature of the metal inside the carbon cages.

After observing the unusual shielding/deshielding effects on the ^{1}H NMR spectrum of the *N*-ethyl pyrrolidinofullerene derivative of $Sc_3N@C_{80}$,[13d] we decided to attach the same pyrrolidine ring adduct to $Y_3N@C_{80}$ to establish the effect of the nature of the trimetallic cluster, if any, on the dramatic shifts observed in the ^{1}H NMR spectrum. It was also interesting to see if changing the nature of the metal would have an effect on the reactivity observed toward the formation of the pyrrolidine adduct. The yttrium-based compound was found to be as reactive as the scandium-based endohedral, and the pyrrolidinofullerene monoadduct was isolated in reasonable yields after 15 min of reaction at 120 °C in a solution of $Y_3N@C_{80}$ with an excess of *N*-ethyl glycine and paraformaldehyde in *o*-dichlorobenzene, as described recently.[13d] MALDI-MS of the main product is shown in Figure 2, with a base peak corresponding to the pyrrolidine monoadduct. Traces of the bis-adduct were also observed by MALDI-MS. Since both monoaddition products reported for $Sc_3N@C_{80}$ (Diels−Alder and pyrrolidine) had reacted at [5,6] double bonds, we assumed that the same was true for $Y_3N@C_{80}$, since the reaction behaved very similarly. Detailed analysis proved this to be wrong.

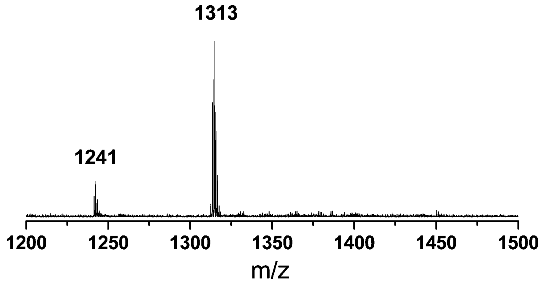


Figure 2. MALDI-MS of $Y_3N@C_{80}$ pyrrolidinofullerene monoadduct. Fragmentation of the parent metallofullerene, $Y_3N@C_{80}$, is observed at 1241 *m/z* under laser desorption.

The ylide addition reaction was also carried out with ^{13}C-enriched (99%) paraformaldehyde, as was done with $Sc_3N@C_{80}$, to investigate the site of reaction and the symmetry of the product. A derivative with ^{13}C-labels at the methylene carbons of the pyrrolidine ring (Scheme 1) was thus obtained.

Unexpectedly, the ^{13}C NMR spectrum of the ^{13}C-enriched yttrium pyrrolidine derivative showed two resonances of equal

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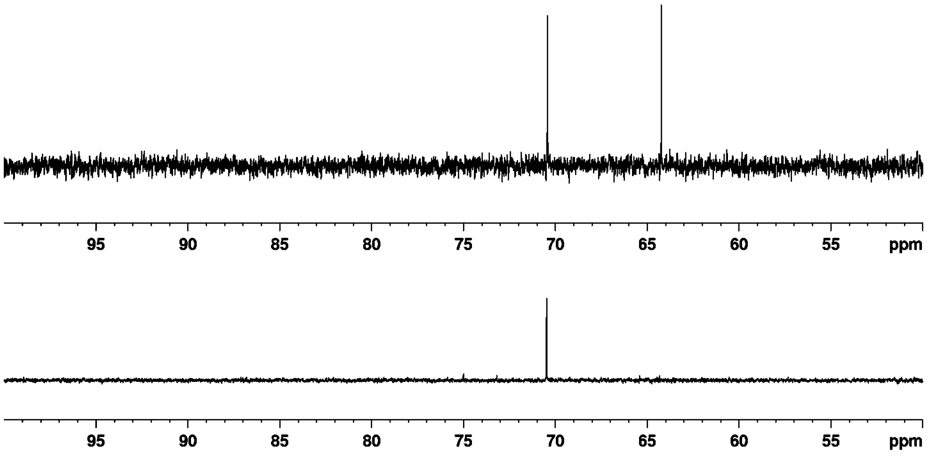


Figure 3. ^{13}C NMR spectra (125 MHz) of the ^{13}C-enriched *N*-ethyl pyrrolidinofullerene derivatives of $Y_3N@C_{80}$ (top) and $Sc_3N@C_{80}$ (bottom).

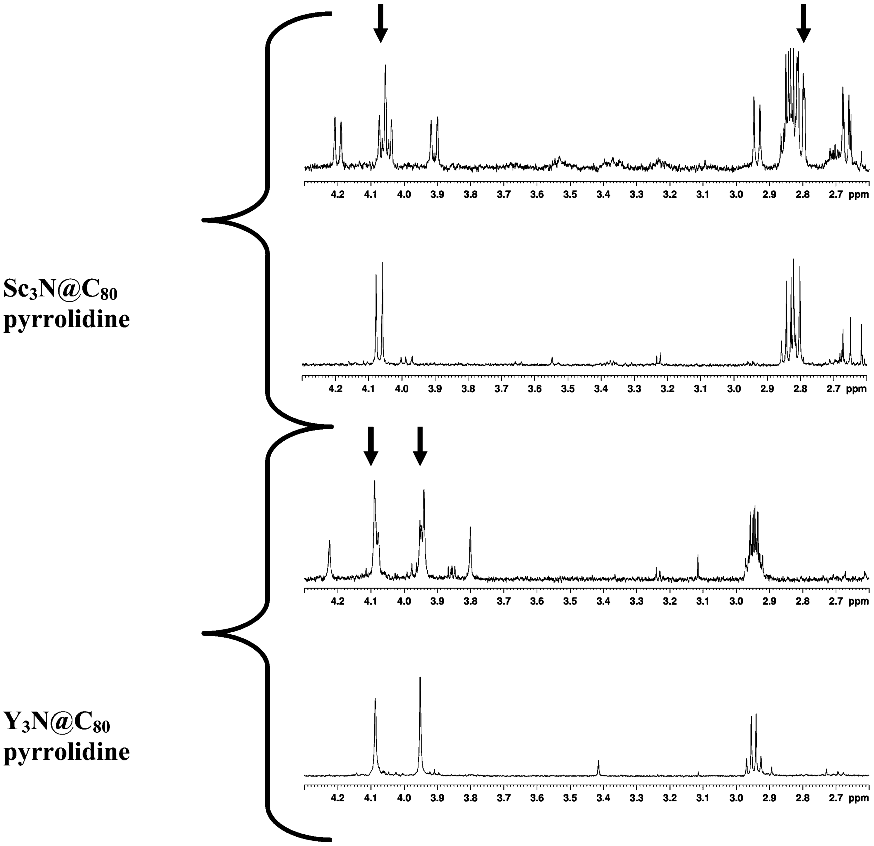


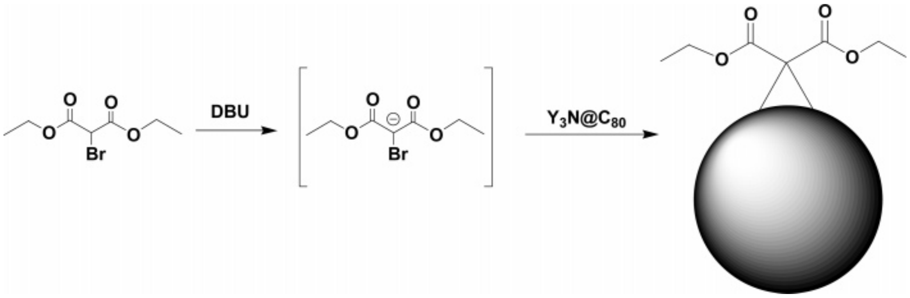
Figure 4. Comparison of the ^{1}H NMR spectra (500 MHz) of the pyrrolidine adducts obtained with ^{13}C-labeled (top spectra) and with unlabeled paraformaldehyde (bottom spectra). The arrows indicate the geminal proton resonances.

intensity at 70.05 and 63.85 ppm, while the ^{13}C-enriched $Sc_3N@C_{80}$ pyrrolidinofullerene analogue exhibited a single signal at 70.09 ppm (Figure 3). The single signal of the scandium derivative indicates that both methylene carbons of the five-membered ring are equivalent and, thus, that there is a plane of symmetry bisecting this ring, similar to what was observed for the Diels−Alder derivative of $Sc_3N@C_{80}$.[13a,b] The observation of two signals for the yttrium pyrrolidinofullerene reveals the presence of nonequivalent pyrrolidine methylene carbons, indicating a different symmetry and suggesting that the cycloadditon occurs at a different site of the icosahedral cage.

The ^{1}H NMR spectrum of the yttrium pyrrolidinofullerene shows that the geminal protons attached to each of the methylene carbons in the ring adduct are equivalent but different from those attached to the opposite carbon. Thus, these geminal hydrogen signals appear as singlets centered at 3.95 and 4.09 ppm. A comparison of the spectra for the yttrium and scandium pyrrolidinofullerenes is shown in Figure 4.

A heteronuclear multiple quantum coherence (HMQC) experiment clearly showed that each of the two nonequivalent carbons in the pyrrolidine ring has two equivalent hydrogens attached (Figure 5). This symmetry is exactly the reverse of that found for the $Sc_3N@C_{80}$ derivative, which has equivalent carbons but nonequivalent geminal hydrogens. The $Y_3N@C_{80}$ derivative has nonequivalent carbons with equivalent geminal hydrogens attached. Therefore, there is symmetry in the front

Scheme 2. Scheme of the Cyclopropanation Reaction of $Y_3N@C_{80}$



and back of the ring where the geminal protons are found, but the two methylene carbons are located in nonsymmetrical positions. This confirms that the cycloaddition does not occur at the [5,6] double bond of the I_h isomer as in the case of the derivatives of $Sc_3N@C_{80}$, and indicates that the addition occurred regioselectively at the [6,6] bond shown in the bottom of Figure 1. Exclusive addition of the pyrrolidine ring at the [6,6] bond results in the observed symmetry.

Since the selectivity is totally different from that observed for $Sc_3N@C_{80}$, we decided to explore a different reaction, one that had repeatedly failed to yield any recoverable products with the scandium endohedral. The reaction is cyclopropanation with excess diethyl bromomalonate and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), as represented in Scheme 2. If the cycloaddition were to occur at the same [6,6] site, the ethyl groups should be in a symmetrical environments and appear as equivalent resonances in the ^1H NMR. If, on the other hand, the addition were to occur at a [5,6] double bond, the ethyl groups would be in nonsymmetrical environments and would appear as nonequivalent triplets and quartets.

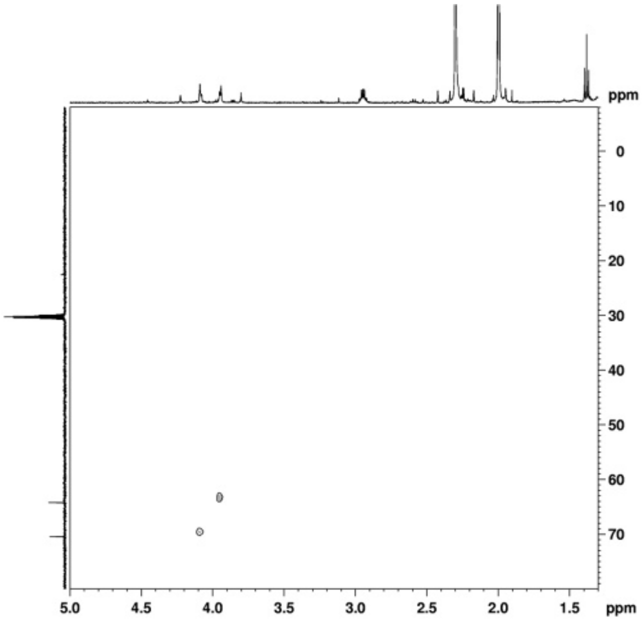


Figure 5. HMQC spectrum of ^{13}C-labeled $Y_3N@C_{80}$ pyrrolidinofullerene.

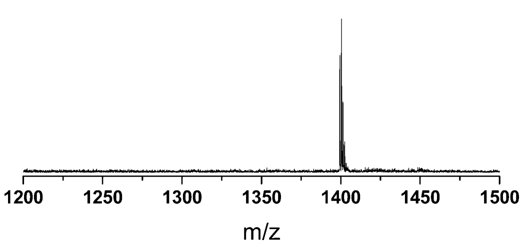


Figure 6. MALDI -MS of malonate monoadduct of $Y_3N@C_{80}$.

The diethyl malonate monoadduct of $Y_3N@C_{80}$ was isolated in reasonable yield after 10 min of reaction at room temperature (Figure 6).

Traces of the bis-adduct were also recovered and identified by MALDI-MS. As mentioned earlier, in our hands this reaction fails completely when conducted with $Sc_3N@C_{80}$, another indication of the dramatic reactivity difference exhibited by the same I_h C_{80} cage dictated by the nature of the endohedral cluster trapped inside the fullerene. The ^1H NMR spectrum of the $Y_3N@C_{80}$-diethyl malonate monoadduct showed a single triplet and a single quartet, indicating that both ethyl groups are equivalent (Figure 7). Therefore, the cyclopropanation occurred regioselectively on the [6,6] double bond of the icosahedral $Y_3N@C_{80}$, as in the case of the 1,3-dipolar addition of *N*-ethylazomethine ylide.

This remarkable difference in reactivity between $Y_3N@C_{80}$ and $Sc_3N@C_{80}$ can only result from the encapsulated cluster, which not only affects the reactivity but also changes the cycloaddition position in a totally regioselective way.

Interestingly, both the cyclopropanation and the 1,3-dipolar cycloaddition reactions were carried out with samples used as received from Luna Innovations without further purification. Thus, the impurities in the starting material do not seem to interfere in the production and isolation of the monoadduct derivatives (Figure 8).

Recently, it has been proposed that the Diels−Alder addition to icosahedral $Sc_3N@C_{80}$ takes place at a [5,6] rather than at a [6,6] bond due to a lower pentagon angle strain resulting from the addition to the coroannulene-type site.[16] If this is true, the C_{80} cage of $Y_3N@C_{80}$ may be distorted so that addition to the [6,6] double bond is preferred. A comparative Raman and infrared spectroscopy study of $Y_3N@C_{80}$ and $Sc_3N@C_{80}$ revealed a more pronounced deviation from the ideal icosahedral symmetry for the yttrium case.[8] This study also found evidence for the formation of intramolecular Sc_3N-C_{80} bonds, specifically between the scandium atoms and the face of the coroannulene subunits of the C_{80} cage. Similar, yet different, intramolecular effects in Y_3N-C_{80} may be responsible for the reactivity differences observed in this study. Further studies with other $M_3N@C_{80}$ species are currently underway in an effort to

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(16) Campanera, J. M.; Heggie, M. I.; Taylor, R. *J. Phys. Chem. B* **2005**, *109*, 4024−4031.

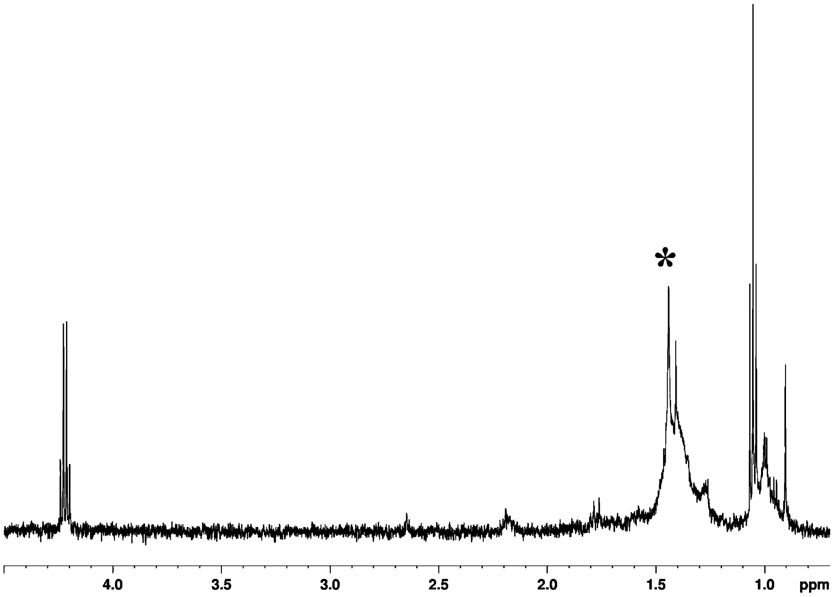

Figure 7. ^{1}H NMR spectrum of the $Y_3N@C_{80}$ diethyl malonate monoadduct. ($*$) denotes impurity due to solvent.

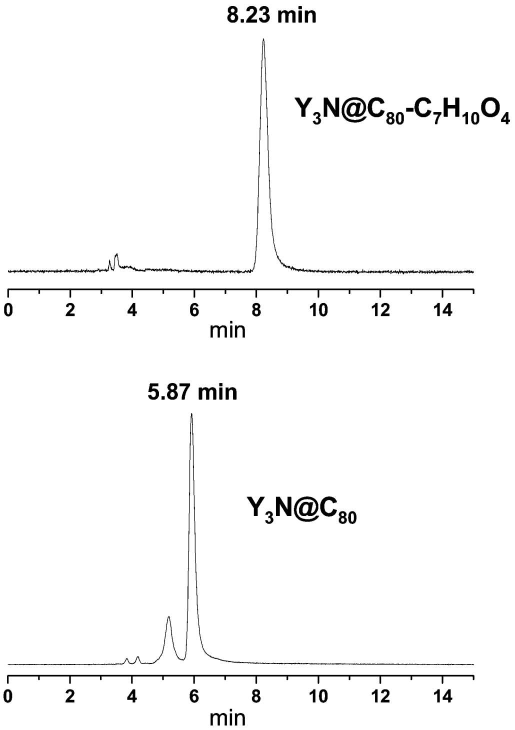

Figure 8. HPLC traces of the diethyl malonate monoadduct product (top) and the $Y_3N@C_{80}$ starting material as received from Luna Innovations (bottom).

unravel the effects due to the endohedral clusters on the properties and reactivities of these interesting compounds.

Conclusions

The same conditions employed for the efficient 1,3-dipolar cycloaddition reaction of *N*-ethylazomethine ylide to $Sc_3N@C_{80}$ to form a monoadduct derivative are successfully applied to $Y_3N@C_{80}$ to produce the first exohedral derivative of this metallofulerene. A second derivative of this material is also prepared via cyclopropanation with diethyl bromomalonate. Both reactions are very selective and yield the same regioisomer monoadduct as the major product. The regioselectivity of the cycloaddition reactions is controlled by the trimetallic nitride cluster. The known exohedral derivatives of $Sc_3N@C_{80}$ contain adducts attached to a [5,6] double bond ring junction (a corannulene-type site), while the cycloaddition reactions with $Y_3N@C_{80}$ occur at a pyrene-type site (a double bond at a [6,6] ring junction) of the icosahedral C_{80} cage. $Y_3N@C_{80}$ also proves to be more reactive toward the Bingel reaction than $Sc_3N@C_{80}$, which does not occur under any attempted reaction conditions.

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Supporting Information Available: Experimental details, COSY spectra of the $Y_3N@C_{80}$-cyclopropanated derivative, as well as complete references. This material is available free of charge via the Internet at http://pubs.acs.org.

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