



Unexpected Formation of Metallofulleroids from Multicomponent Reactions, with Crystallographic and Computational Studies of the Cluster Motion

Yanbang Li, Thomas J. Emge, Antonio Moreno-Vicente, William P. Kopcha, Yue Sun, Iram F. Mansoor, Mark C. Lipke, Gene S. Hall, Josep M. Poblet, Antonio Rodríguez-Forteza,* and Jianyuan Zhang*

Abstract: New multicomponent reactions involving an isocyanide, terminal or internal alkynes, and endohedral metallofullerene (EMF) $\text{Lu}_3\text{N}@C_{80}$ yield metallofulleroids which are characterized by mass-spectrometry, HPLC, and multiple 1D and 2D NMR techniques. Single crystal studies revealed one ketenimine metallofulleroid has ordered Lu_3N cluster which is unusual for EMF monoadducts. Computational analysis, based on crystallographic data, confirm that the endohedral cluster motion is controlled by the position of the exohedral organic appendants. Our findings provide a new functionalization reaction for EMFs, and a potential facile approach to freeze the endohedral cluster motion at relatively high temperatures.

Endohedral metallofullerenes (EMFs) are a family of molecules with special host-guest structures that allow chemists to manipulate encapsulated metal ions with the arsenal of organic chemistry,^[1] for potential applications^[2] including single-molecule magnets,^[3–5] spin-quantum computing,^[6,7] artificial photosynthesis,^[8] dynamic nuclear polarization,^[9] magnetic resonance imaging (MRI) contrast agents,^[10] and therapeutic agents.^[11,12] To unleash the power to do so, the development of new reactions for EMFs has been an ongoing task. A subgroup of EMF, the nitride clusterfullerenes (NCFs),^[13,14] especially the most abundant members $\text{M}_3\text{N}@I_h\text{-C}_{80}$, have very high stability^[15] that gives them high production yields, but meanwhile makes their chemical modification challenging. With notable exceptions,^[16–20] most reactions of the NCFs with well-characterized derivatives are from cycloadditions, including the Bingel–Hirsch reaction,^[21] Prato reaction,^[22,23] Diels–Alder reaction,^[24] diazo addition,^[25,26] benzyne addition,^[27,28] and reaction with azide^[29]

or ylide.^[30] Overall, the pool of viable reactions on NCFs remains very limited; new reactions, and especially those not directly inspired from an analogous C_{60} reaction, are still in strong demand.



Multicomponent reactions can introduce functional groups from different reactants, and are therefore valuable for materials synthesis. While the 1,3-dipolar “Prato” reaction is a case in point, such reactions are rare for NCFs. Isocyanides and alkynes are a pair of widely used reactants to generate ring structures in organic synthesis,^[31,32] working mainly for internal alkynes, but in a couple of cases, also for terminal alkynes.^[33,34] In the multicomponent reactions, an isocyanide (e.g., $^1\text{BuNC}$, Figure 1a) reacts with an alkyne bearing at least one electron-withdrawing group (EWG) to generate a reactive species, represented by two resonance forms (Figure 1a): a 1,4-dipole (**A**), and a 1,3-dipole (**B**), which can undergo cycloadditions with a third reactant. One precedent of the isocyanide-based multicomponent reaction on C_{60} was reported to yield a [3+2] product related to resonance form **B**, and a [2+2] product not related to either resonance form.^[35] Here we report the first isocyanide-based multicomponent reactions on EMFs, among $^1\text{BuNC}$, various alkynes, and $\text{Lu}_3\text{N}@I_h(7)\text{-C}_{80}$ (one of the most inert NCFs,^[36] shortened as $\text{Lu}_3\text{N}@C_{80}$ hereafter), that unexpectedly formed metallofulleroids with [6,6]-open structures. Remarkably, a ketenimine metallofulleroid has highly ordered cluster in its single crystal at 120 K, suggesting the exohedral appendant raised the energy barrier of endohedral cluster rotation, as confirmed by computations.

Multicomponent reactions on the EMF were first carried out with $\text{Lu}_3\text{N}@C_{80}$, $^1\text{BuNC}$ and EWG-bearing terminal alkynes **1a–c** (Figure 1b). In each reaction, a major product was identified by HPLC, and purified as **2a–c**. However, disubstituted internal alkynes **1d–f** did not yield any products, even with highly electron withdrawing $-\text{CF}_3$ group. As the reactions of **1d–f** with isocyanides to form reactive intermediates have been observed before,^[33,34,37] we ascribe the unreactivity of **1d–f** to the failed addition of the intermediates to the $\text{Lu}_3\text{N}@C_{80}$ cage. Notably, the same reactions were also performed on C_{60} and none of **1a–f** resulted in an isolatable product, whether air or an inert atmosphere was used.

Products **2a–c** were purified by flash chromatography, and the purity was confirmed by HPLC on 5PYE and Buckyprep-D columns. Full spectroscopic characterizations were then performed for **2a–c** (Figures S1–S26). Matrix-assisted laser desorption ionization time-of-flight mass-spectroscopy

[*] Dr. Y. B. Li, Dr. T. J. Emge, W. P. Kopcha, Y. Sun, I. F. Mansoor, Dr. M. C. Lipke, Dr. G. S. Hall, Dr. J. Zhang
 Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey
 123 Bevier Rd, Piscataway, NJ 08854 (USA)
 E-mail: jy.zhang@rutgers.edu

Dr. A. Moreno-Vicente, Dr. J. M. Poblet, Dr. A. Rodríguez-Forteza
 Departament de Química Física i Inorgànica, Universitat Rovira i Virgili
 Marcel·lí Domingo 1, 43007 Tarragona (Spain)
 E-mail: antonio.rodriguez@urv.cat

 Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
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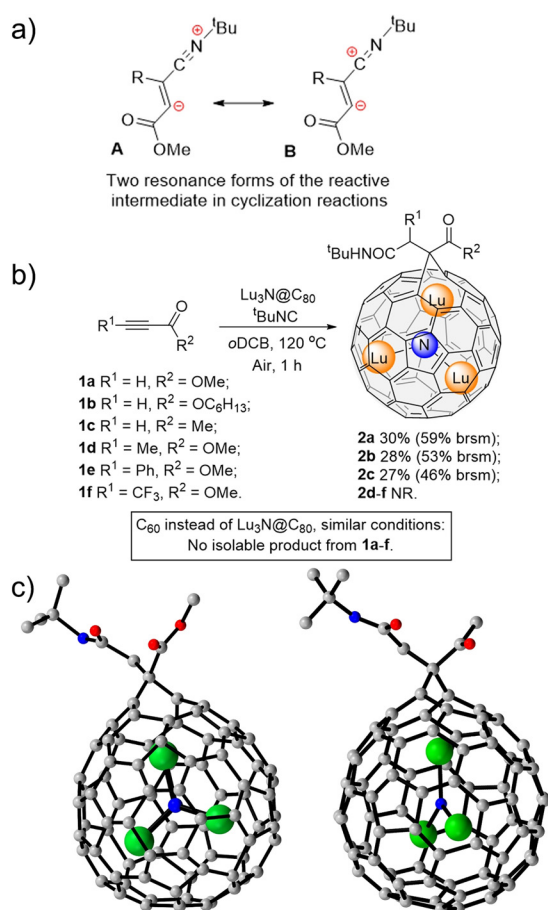


Figure 1. Reactions between an alkyl isocyanide and an alkyne. a) Reactive species formed. b) Preparation of **2a–c**. brsm = based on recovered starting material; NR = No reaction. c) Single-crystal X-ray structure of compounds **2a** (left) and **2c** (right).^[53]

(MALDI-TOF MS) of **2a–c** gave clear molecular ions corresponding to a mass of three reactants plus one molecule of water (either from air or moisture in the chemicals). According to NMR, structures of **2a–c** (Figure 1b) were elucidated as [6,6]-open metallofulleroids, based on the following clues: ¹H NMR spectra show two pairs of non-equivalent doublets (**2a**: 3.87, 3.78 ppm, ²J_{HH} = 15.6 Hz; **2b**: 3.93, 3.82 ppm, ²J_{HH} = 15.5 Hz; **2c**: 3.65, 3.57 ppm, ²J_{HH} = 15.6 Hz) indicating methylene with hindered bond rotation; ¹³C NMR spectrum of **2b** exhibits 73 distinct signals in the aromatic region, and 2 signals around 90 ppm at the reaction site for the C₈₀ cage,^[25,38] showing a complete loss of symmetry (theoretically 78 aromatic peaks, but they are often not completely resolved, as seen in other [6,6]-open C₈₀ structures^[25,38–40]); similarity of the UV-vis-NIR spectra of **2a–c** with precedents^[21,25,26,41] of [6,6]-open M₃N@C₈₀ adducts; C–H connections obtained from other 1D and 2D NMR approaches (DEPT-¹³C, HMQC, HMBC). Finally, single crystal X-ray diffraction analysis (Figure 1c) of **2a** and **2c** unambiguously confirmed the [6,6]-open structures, with one Lu³⁺ ion associated with the opening site. The other two Lu³⁺ ions have clear disorder in the crystal structure which indicates cluster rotation inside the cage. The net result of the reaction, instead of a [3+2] addition, is an anion-induced

cyclopropanation, similar to a Bingel–Hirsch process,^[21] followed by electron movement to form a ketenimine which is subject to instantaneous hydration on the C=N double bond.

Despite the unreactivity of internal alkynes **1d–f**, dimethyl acetylenedicarboxylate (DMAD) **3** turned out to be a surprising exception. Under similar condition (Figure 2a), a pure product was obtained and spectroscopically characterized (Figures S27–S37), and thereby identified as ketenimine metallofulleroid **4** with the same [6,6]-addition with **2a–c** (except the hydration did not occur). The structure was then definitively confirmed by its single crystal X-ray diffraction analysis (Figure 2b). The addition pattern is drastically different from the reported C₆₀ reaction with the same reactants.^[35]

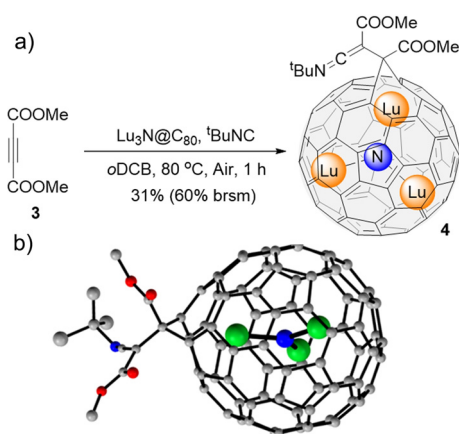


Figure 2. Synthesis and characterization of **4**. a) The reaction Scheme. b) Single-crystal X-ray structure of **4**.

In retrospect, while the ketenimine appendant (or its hydrated version) is unprecedented for EMFs, the only analogous reaction in literature was the PPh₃-induced addition that specifically worked with diester internal alkynes, forming zwitterionic derivatives of C₆₀^[42,43] and monometallic EMF Dy@C₈₂.^[44] Indeed, the reaction did not work the same way for terminal alkynes: when PPh₃ reacted with terminal alkynes and C₆₀, an annulated bismethanofullerene adduct of two molecules of alkynes and C₆₀ would form via a [2+4+2] addition, and PPh₃ was not part of the product.^[45] In light of this, we tried PPh₃ instead of ^tBuNC as the nucleophile in our reactions with Lu₃N@C₈₀, and found that the addition pattern is also dependent on the alkynes. With internal alkyne **3**, a zwitterionic metallofulleroid (compound **S1** in SI) was formed (Figures S38–S41). With terminal alkyne **1a**, on the other hand, only a bismethano-EMF (compound **S2** in SI) was obtained (Figures S42, S43). In comparison, the isocyanide-induced reactions yield more consistent product form, not sensitive to air, and are more practical to introduce functional groups from different reactants, which is a key advantage of multicomponent reactions.

Notably, the crystal of **4** showed an ordered endohedral Lu₃N cluster at 120 K, which is different from **2a**, **2c**, and most reported NCF monoadducts. The notable exceptions are when there is explicit charge transfer between the EMF cage

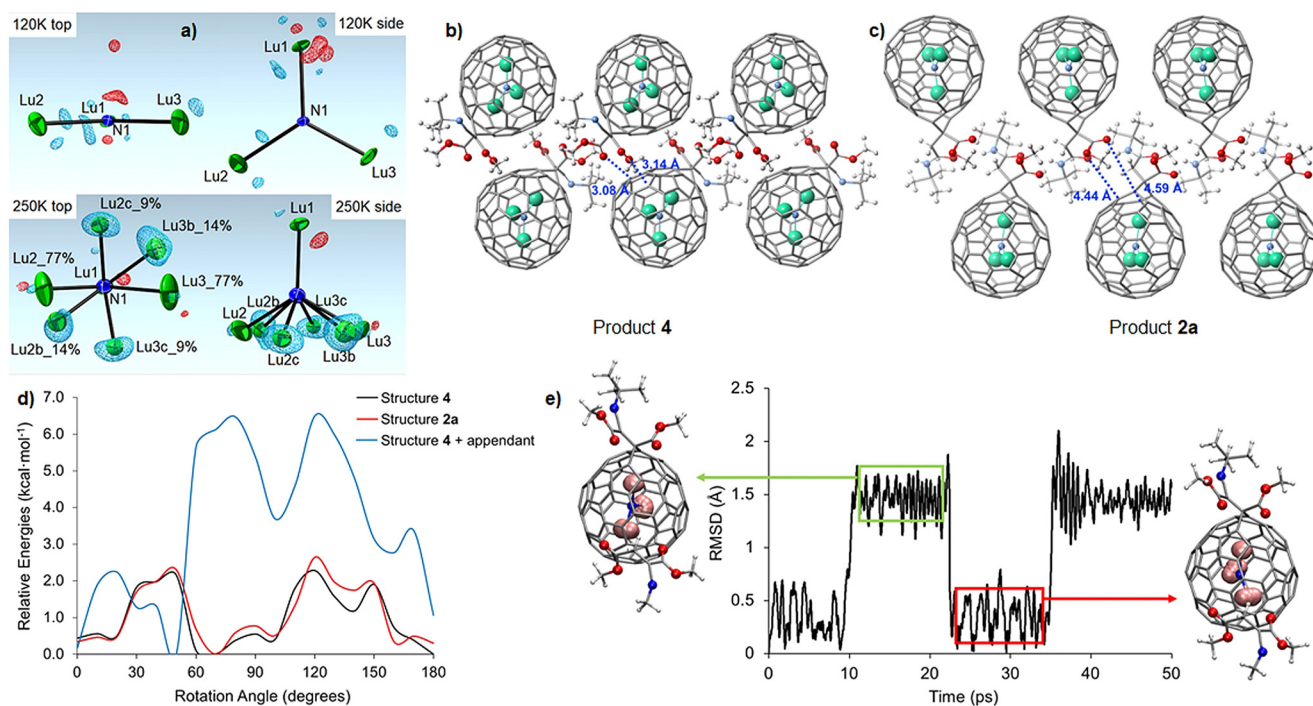


Figure 3. Low endohedral cluster motion of **4** due to the existence of the exohedral organic appendant. a) Orthogonal views of the difference electron density within 3 Å of the Lu₃N centroid at 120 K (top) and at 250 K (bottom), with ellipsoids drawn at the 50% probability level. b) and c) Crystal packings of products **4** and **2a**, respectively, showing the shortest C...O contacts (in blue) between the fullerene cage and the O atom of the neighboring organic appendant. d) Energy profiles (in kcal mol⁻¹) for the rotation of the internal Lu₃N cluster around the Lu1-N axis (see text) for structure **4** (black), structure **2a** (red) and structure **4** together with the appendant of a neighboring molecule (blue). e) Root mean square deviation (RMSD) along the 50 ps trajectory of the Car-Parrinello simulation of product **4** interacting with the appendant of a neighboring molecule in the solid state.

and the functional group (e.g., an acid-base pair).^[20,46] This is a feature typically seen in the synthetically challenging multi-adducts of NCFs which, understandably, has ordered clusters fixed by multiple organic groups.^[47,48] The crystal of **4** was further studied at different temperatures. First, at 120 K, the final difference density map reveals ordered sites for all cluster atoms (Figure 3a, top). Upon raising the temperature to 250 K, the Lu atom close to the organic appendant (Lu1) and the N atom remain ordered at their 120 K sites; however, the other two original Lu sites were found to have 80% occupancy (Lu2A and Lu3A) and four additional sites were observed, suggesting cluster motion. If the electron density contributions of these four sites are omitted in a difference density map using the 250 K results and X-ray data of **4** (Figure S44), Figure 3a (bottom) obtained (all ellipsoids included). Upon further raising the temperature from 250 K to 298 K, no additional site disorder of Lu atoms was observed.

These results show that the cluster motion of **4** started at higher temperature than most M₃N@C₈₀ monoderivatives and may not have fully free cluster motion even at room temperature. We hypothesize the abnormal behavior is caused by the ketenimine functional group which is new for EMFs. Careful inspection of the molecular packing in the solid state suggests that in **4** short contacts around 3.1 Å exist between the EMF cage and the O atoms of the carbonyl groups of the appendant from an adjacent molecule (Figure 3b). Interestingly, these contacts are found in a region of

the cage near one of the Lu atoms that could in principle rotate, i.e., not Lu1 that points to the appendant. In contrast, the shortest contacts between EMF cages and appendant of adjacent molecules in **2a** are as long as 4.5 Å and in a region around Lu1 (Figure 3c). Therefore, it can be inferred that these shorter contacts in **4** are at the origin of the hindered cluster motion, as also suggested by a theoretical study where the cluster motion in pristine NCFs is controlled externally.^[49] Further fundamental understanding was gained with DFT calculations using the PBE functional (Figure S45 and detailed method in SI). For the rotation of the Lu₃N cluster around the Lu1-N axis, similar energy profiles were found in products **2a** and **4** with quite low energy barriers (around 2.5 kcal mol⁻¹, Figure 3d). However, when the appendant of the neighboring molecule is considered in the computation, as is the case in the solid state, remarkably, the barrier for the rotation is significantly increased to 6–7 kcal mol⁻¹ (Figure 3d), which confirms our hypothesis. Besides, Car-Parrinello molecular dynamics (CPMD) simulations (Figure S46 and detailed method in SI) for product **4** also considering the appendant of a neighbor molecule at 120 K (50 ps-long trajectory) showed that one Lu atom is interacting alternatively back and forth with the two carbonyl O atoms of the dicarboxylate. This interaction restricts the Lu atoms to that very limited region and, therefore, hinders free cluster rotation (Figure 3e).

Analysis of the molecular orbitals of product **4** also revealed that the HOMO and LUMO are essentially local-

ized on the carbon cage (Figure S47), in line with the similar first oxidation and reduction potentials of **2a**, **4**, and reactant $\text{Lu}_3\text{N@C}_{80}$ (Table S1, Figure S48).

Finally, the reaction mechanism was studied by DFT calculations (Figure 4). In short, the reaction started with a barrierless anionic attack (Figure S49) of the dipole (Figure 1a) to a C atom in a triple hexagon junction (THJ) of $\text{Lu}_3\text{N@C}_{80}$, to form intermediate **I** in a rather exothermic process (-27.4 kcal mol $^{-1}$). Afterwards, intermediate **I** undergoes 3-*exo*-trig ring closure to form product **2a'** overcoming a small barrier of 2.3 kcal mol $^{-1}$, which is significantly lower than the barrier for the ring closure in a Bingel–Hirsch reaction.^[50,51] The **TS**₂ shows a C–C distance for the forming bond of 2.05 Å. The C–C distance for the broken bond that gives the open structure is 1.65 Å. Product **2a'** is 7.0 kcal mol $^{-1}$ more favorable than **5**, a [3+2] product from 5-*exo*-dig process, which is not observed in EMF reactions. Hydration would then yield the isolated product **2a**. Based on these results, the complete mechanism for both reactions is proposed in Figure S50.

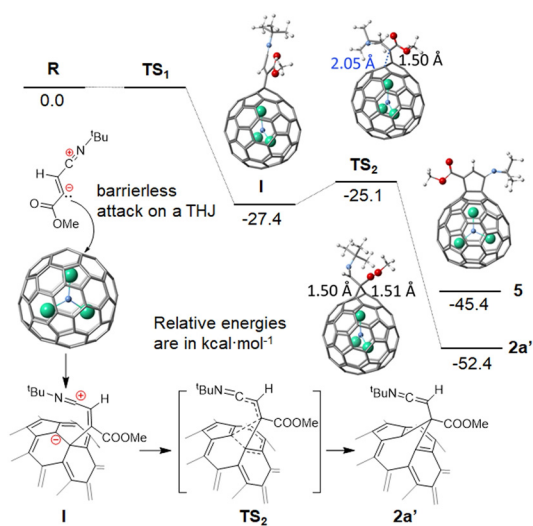


Figure 4. Reaction pathway for the formation of **2a'**.

In conclusion, a new multi-component reaction of *t*-butyl isocyanide, an alkyne, and NCF $\text{Lu}_3\text{N@C}_{80}$ has been investigated. A series of unexpected [6,6]-open metallofulleroids, **2a–c** and **4** were obtained and fully characterized. Notably, **4** showed significantly hindered cluster motion caused by the close interaction with the exohedral organic appendant of a neighboring molecule, as observed in single-crystal study, and for the first time rationalized by DFT computation and CPMD simulation. Given $\text{Lu}_3\text{N@C}_{80}$ is one of the most inert clusterfullerenes, it is foreseeable that this new reaction could also work on other clusterfullerenes (e.g., metal carbide, oxide, sulfide, cyanide EMFs),^[52] even though the products might depend on the charge transfer and the size of the cluster. Additionally, our work provides a new approach to achieve a static solid-state cluster in an NCF by a facile, one-step reaction, which can open avenues to many new research directions, from potential regioselectivity in further reactions,

to the development of quantum information materials with well-defined orientation of magnetic clusters.

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Conflict of Interest

The authors declare no conflict of interest.

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