Ring-Opened Fullerenes: An Unprecedented Class of Ligands for Supramolecular Chemistry**

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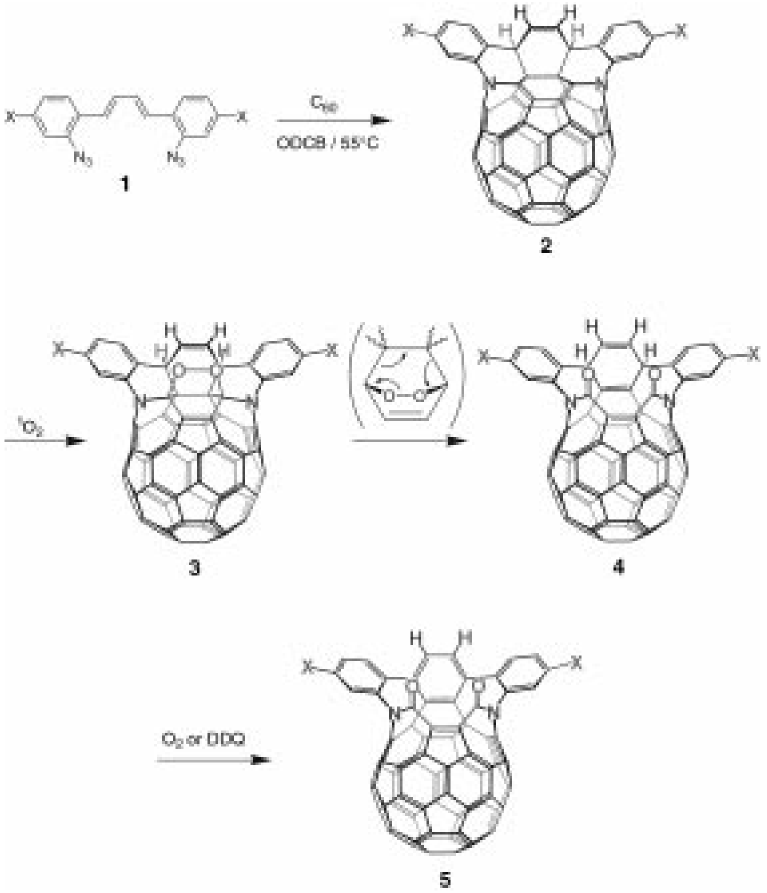
Whereas the outer sphere chemistry of C_{60} and the higher fullerenes has been extensively investigated,[1] the internal cavities of these carbon cages have been scarcely considered, even though they are large enough to hold any atom or small molecule.[2] This situation is mainly associated with the difficulties of preparing endohedral fullerene complexes on a truly preparative scale. In the past few years, successful incorporation of rare gases or atomic nitrogen into the C_{60} cage has been achieved with incorporation ratios of up to 0.1 % by pressure/heating or plasma reactions. Several endohedral metallofullerenes have also been obtained by the evaporation of graphite/metal oxide or carbide composites. Although their preparation constitutes a remarkable achievement, the small quantities of material obtained after tedious HPLC separations appear to be a severe limitation for the exploration of this whole new world of fullerene chemistry. Therefore, a stimulating challenge for the organic chemists is the development of efficient synthetic approaches for the preparation of endohedral fullerene complexes. An immediate choice is to use the existing framework of fullerenes and create an opening wide enough to allow an atom or a small molecule to pass through before closing it back. However, the formation of an effective aperture on the surface of fullerenes has proven to be very difficult;[3] the pioneering research in this area has been summarized by Rubin in an excellent review article.[4]

In the last two years, key advances have been reported within this field by the research group of Rubin,[5, 6] and this innovative work will be briefly presented here. It must also be mentioned that Stevenson et al. believed they were successful in the preparation of endohedral ring-opened fullerene complexes, however, further investigations revealed that it was actually not the case.[7]

The formation of an effective opening within the C_{60} core has been achieved by an original reaction sequence in which four bonds of the fullerene cage are cleaved (Scheme 1).[5] The reaction of diazidobutadiene **1** with C_{60} followed by N_2 extrusion afforded iminofullerene derivative **2**. Subsequent reaction with singlet oxygen yielded an endoperoxide intermediate **3**, which rearranged by spontaneous [2+2+2] ring opening to generate **4**. Finally, treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or oxygen afforded the dehydrogenation product **5**. This unique one-pot reaction provided efficient formation of the largest orifice created so far on the C_{60} molecule, thus providing the opportunity to test if small atoms or molecules could be made to pass through it.



Scheme 1. Preparation of ring-opened fullerene **5**. ODCB = *ortho*-dichlorobenzene, X = *t*Bu.

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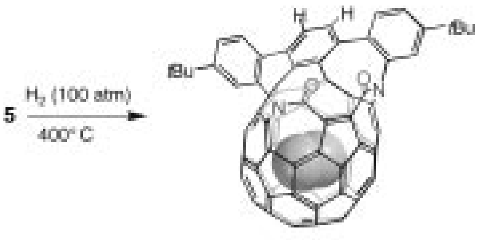
Incorporation experiments were first carried out with helium.[6] Careful ^{3}He NMR investigations provided a fully convincing demonstration of the incorporation of a He atom inside the ring-opened fullerene **5**. The formation of the host–guest complex He@**5** was found to occur even at low helium pressure, and the fraction incorporated under a pressure of 3–4 atm (0.05 %) approaches that of He@C_{60} (0.1 %) prepared by the direct high-pressure method.[8] Treatment of compound **5** at 400 °C under a H_2 pressure of 100 atm for 48 h also allowed the incorporation of molecular hydrogen inside a fraction of the ring-opened compound (Scheme 2).



H_2@**5**

Scheme 2. Incorporation of molecular hydrogen inside the ring-opened fullerene **5**.

Unambiguous demonstration of the presence of molecular hydrogen inside the ring-opened fullerene **5** was obtained from careful NMR experiments. It must be pointed out that the fraction of H_2@**5** thus produced was found to be as high as 5 %, which is by far the highest amount of direct incorporation obtained for any gas in a fullerene.

With the formation of a large orifice in the C_{60} core and the successful insertion of He and H_2, two critical steps have been realized towards the development of an efficient synthetic approach for the preparation of endohedral fullerene complexes. The ring-opened fullerene **5** is also the first member of a new class of ligands for host–guest chemistry, and the preparation of endohedral ring-opened fullerene complexes paves the way for the preparation of original supramolecules. In addition, endohedral lanthanide–fullerene derivatives are good candidates for conventional diagnostic radiology (MRI contrast and X-ray imaging agents) as a consequence of the effective isolation of the internal metal from its surroundings and the absence of any release of the free metal in vivo.[9] Endohedral lanthanide ring-opened fullerenes could be, therefore, an interesting alternative to endohedral metallofullerenes for biomedical applications since they should be easier to prepare on a truly preparative scale.

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[6] Y. Rubin, T. Jarrosson, G.-W. Wang, M. D. Bartberger, K. N. Houk, G. Schick, M. Saunders, R. J. Cross, *Angew. Chem.* **2001**, *113*, 1591–1594; *Angew. Chem. Int. Ed.* **2001**, *40*, 1543–1546.

[7] The strategy explored by the research group of Stevenson for the preparation of endohedral fullerene complexes is based on the synthesis of a [2+2] cycloaddition product of C_{60} followed by ring opening through a retrocycloaddition reaction to provide a passageway to the interior of the fullerene. They claimed on the basis of EPR data alone that they were able to prepare endohedral alkali metal fullerene complexes starting from the [2+2] C_{60}–cyclooctatetraene adduct: C. D. Stevenson, J. R. Noyes, R. C. Reiter, *J. Am. Chem. Soc.* **2000**, *122*, 12905–12906. However, a few months later an addition/correction to the original paper was published: the prepared compound was not an endohedral fullerene derivative (*J. Am. Chem. Soc.* **2001**, *123*, 4372).

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