Isolation and Characterization of a Carbene Derivative of $La@C_{82}$

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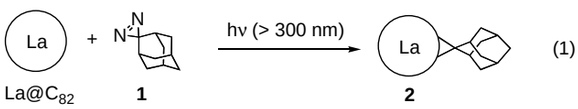
Endohedral metallofullerenes encapsulate one or more metal atoms inside a hollow fullerene cage. These fullerenes have attracted special attention, because they engender new spherical molecules with unique electronic properties and structures that are unexpected for empty fullerenes.[1] The recent successful isolation and purification of endohedral metallofullerenes have encouraged the investigation of their physical and chemical properties. It would be of interest to understand how the chemical reactivity and selectivity of empty fullerenes change upon endohedral metal doping, and how the electronic properties of endohedral metallofullerenes change upon reduction, oxidation, and chemical functionalization. We now present the first instance of an isolation and crystallographic characterization of an paramagnetic endohedral monometallofullerene derivative from the selective $La@C_{82}$ reaction.

Irradiation of 1,2,4-trichlorobenzene/toluene solution of $La@C_{82}$[8] (4.3 mg, 1.9×10^{-4} M) and an excess molar amount of **1** in a degassed sealed tube at room temperature using a high-pressure mercury-arc lamp (cutoff < 300 nm) resulted in the formation of the adduct,



$La@C_{82}$ **1** **2** (1)

$La@C_{82}$(Ad) (**2**, Ad = adamantylidene) in 80% yield, which was purified by preparative HPLC (Equation 1).

Finally, the X-ray analysis unambiguously characterizes the isomer type of the fullerene cage and locates the La atom at a single site near the end of the molecule, as shown in Figure 1.

Our study of the highly selective derivatization of $La@C_{82}$ indicates that encapsulating metal is useful for controlling the reactivity and selectivity of fullerenes.

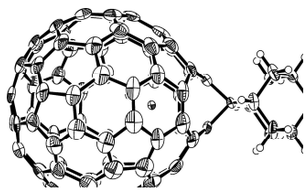


Figure 1. ORTEP drawing of one enantiomeric isomer of $La@C_{82}$(Ad) (**2**) showing thermal ellipsoids at the 50% probability level. The CS_2 molecules are omitted for clarity.

Reference

(1) *Endofullerenes: A New Family of Carbon Clusters*; Akasaka, T., Nagase, S. Eds.; Kluwer Academic Publisher: Dordrecht, 2002.