Isolation and Characterization of a CarbeneDerivative of 
La@C_{60}

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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. 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_{60} reaction. Irradiation of 1,2,4-trichlorobenzene/toluene solution of La@C_{60} 2 (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,

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\begin{align*}
\text{La@C}_{60} + 1 & \xrightarrow{hv (> 300 \text{ nm})} \text{La@C}_{60}(\text{Ad}) \quad \text{(1)}
\end{align*}
\]

La@C_{60}(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_{60} indicates that encapsulating metal is useful for controlling the reactivity and selectivity of fullerenes.

Reference