

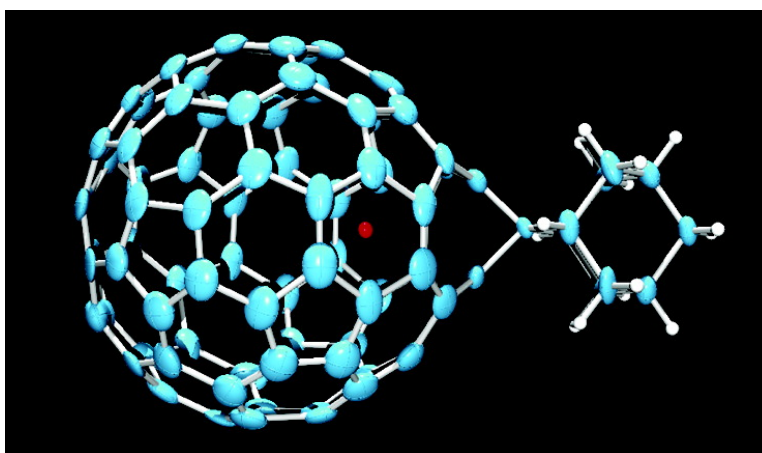
Communication

## Isolation and Characterization of a Carbene Derivative of La@C

Yutaka Maeda, Yoichiro Matsunaga, Takatsugu Wakahara, Satomi Takahashi, Takahiro Tsuchiya, Midori O. Ishitsuka, Tadashi Hasegawa, Takeshi Akasaka, Michael T. H. Liu, Kisato Kokura, Ernst Horn, Kenji Yoza, Tatsuhisa Kato, Shingo Okubo, Kaoru Kobayashi, Shigeru Nagase, and Kazunori Yamamoto

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## Isolation and Characterization of a Carbene Derivative of La@C<sub>82</sub>

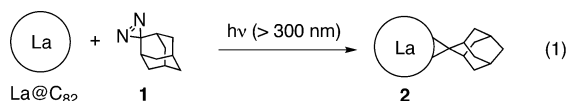
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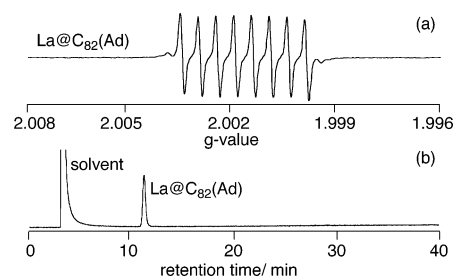
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Endohedral metallofullerenes encapsulate one or more metal atoms inside a hollow fullerene cage. These fullerenes have attracted special attention because they engender new spherical molecules with unique electronic properties and structures that are unexpected for empty fullerenes.<sup>1,2</sup> 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<sup>3,4</sup> and how the electronic properties of endohedral metallofullerenes change upon reduction, oxidation,<sup>5</sup> and chemical functionalization. Dorn and co-workers reported the selective formation of a diamagnetic Sc<sub>3</sub>N@C<sub>80</sub> adduct via a Diels–Alder reaction.<sup>4b,c</sup> Our earlier report indicated that the high reactivity of endohedral metallofullerenes may be ascribed to their electronic properties.<sup>4–7</sup> The ESR spectra measured during the reaction reveal the formation of several regioisomers with different La isotopic splittings.<sup>3,4a</sup> In contrast, the regioselective addition reaction of La@C<sub>82</sub> with 2-adamantane-2,3-[3H]-diazirine (**1**) affords the first single isomer which has been successfully isolated. We now present the first instance of an isolation and crystallographic characterization of a paramagnetic endohedral monometallofullerene derivative from the selective La@C<sub>82</sub> reaction.

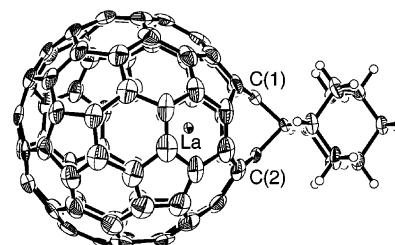
Irradiation of 1,2,4-trichlorobenzene/toluene solution of La@C<sub>82</sub><sup>8</sup> (4.3 mg, 1.9 × 10<sup>-4</sup> M) and an excess molar amount of **1** in a degassed sealed tube at room temperature using a high-pressure mercury-arc lamp (cutoff < 300 nm) resulted in the formation of the adduct, La@C<sub>82</sub>(Ad) (**2**, Ad = adamantylidene), in 80% yield, which was purified by preparative HPLC (eq 1). Figure 1 shows



the ESR spectrum and HPLC profile of isolated **2**. MALDI-TOF mass spectrometry of adduct **2** (C<sub>92</sub>H<sub>14</sub>La, mass *m/z* 1257) exhibits a molecular ion peak at *m/z* 1260–1257 and a peak at *m/z* 1126–1123 (La@C<sub>82</sub>) due to the loss of the Ad group. The UV–visible–



**Figure 1.** (a) ESR spectrum of isolated La@C<sub>82</sub>(Ad) (**2**) (hfcc: 0.89 G, *g*-value: 2.0018). (b) HPLC profile of isolated La@C<sub>82</sub>(Ad) (**2**) (Buckyprep column, φ 4.6 mm × 250 mm, toluene 1 mL/min).



**Figure 2.** ORTEP drawing of one enantiomeric isomer of La@C<sub>82</sub>(Ad) (**2**) showing thermal ellipsoids at the 50% probability level. The CS<sub>2</sub> molecules are omitted for clarity.

near-infrared absorption spectrum of **2** is similar to that of the pristine La@C<sub>82</sub>. These results suggest that **2** retains the essential electronic and structural character of La@C<sub>82</sub>. Finally, the X-ray analysis<sup>9</sup> 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 2. The C(1)···C(2) distance is 2.097 Å, indicative of the open structure. The La···C(1) and La···C(2) distances are 2.658 and 2.634 Å, respectively. These agree well with the calculated values; the C···C distance is 2.118 Å, and the La···C distances are 2.722 and 2.690 Å.<sup>10</sup> Although it has been reported that multiple sites for the metal atoms are found in the structures of the related C<sub>82</sub> endohedrals such as Er@C<sub>82</sub>,<sup>11</sup> interestingly and surprisingly, a comparison of X-ray data collected at 90, 213, and 293 K reveals that the La atom remains in the same position, as shown in Figure 2.

Since there are 24 non-equivalent carbons and 19 non-equivalent 6–6 bonds in La@C<sub>82</sub>, addition may take place at several sites to afford a large number of possible monoadduct isomers. The reaction of La@C<sub>82</sub> with disilirane<sup>3</sup> or phenyldiazomethane<sup>4a</sup> gave several 1:1 adduct isomers. The remarkable change of selectivity in the

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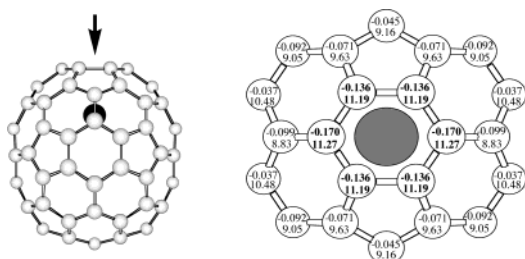
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**Figure 3.** Selected charge densities (upper) and POAV ( $\theta_{\Delta\pi}-90^\circ$ ) values (lower) in La@C<sub>82</sub>.

**Table 1.** Redox Potentials (V),<sup>a</sup> Ionization Potentials (eV), and Electron Affinities (eV) of La@C<sub>82</sub> and La@C<sub>82</sub>(Ad)

compd	oxE <sub>2</sub> <sup>b</sup>	oxE <sub>1</sub>	redE <sub>1</sub>	redE <sub>2</sub>	redE <sub>3</sub>	Ip/Ea
La@C <sub>82</sub>	+1.07	+0.07	-0.42	-1.37	-1.53	6.19/3.38
La@C <sub>82</sub> (Ad)	+1.01	-0.01	-0.49	-1.44	-1.79	5.97/3.24

<sup>a</sup> Versus Fc/Fc<sup>+</sup>. In 1,2-dichlorobenzene with 0.1 M (*n*-Bu)<sub>4</sub>NPF<sub>6</sub> at a Pt working electrode. CV: scan rate, 20 mV s<sup>-1</sup>. <sup>b</sup> Values were obtained by DPV: pulse amplitude, 50 mV; scan rate, 20 mV s<sup>-1</sup>.

reaction of La@C<sub>82</sub> with **1** is the first example of the selective reaction of endohedral metallofullerenes.

Photolysis of **1** has been used to generate adamantylidene (**3**) and diazoadamantane (**4**).<sup>12,13</sup> The formation of **2** can be explained in terms of the reaction of **4** with La@C<sub>82</sub>. Pezacki et al. reported the formation of **4** from 5',5'-dimethoxyspiro[adamantane]-2,2'-[Δ<sup>3</sup>-1.3.4-oxadiazoline] (**5**) on the basis of their laser flash photolysis studies of **5**.<sup>14</sup> To clarify the mechanism of the reaction of La@C<sub>82</sub> with **1**, we studied the reaction of C<sub>60</sub> with **5**. Irradiation of **5** in the presence of C<sub>60</sub> produced only the fulleroid, suggesting its formation via the reaction of **4** with C<sub>60</sub>.<sup>15</sup> This result indicates that **5** generates **4**, not **3**. Irradiation of **5** in the presence of La@C<sub>82</sub> did not give **2**, indicating that the diazo compound **4** is not the intermediate in the formation of **2**. The local strain on each carbon atom of fullerenes plays an important role in determining their reactivity.<sup>16</sup> The pyramidalization angles from the p-orbital axis vector analysis POAV ( $\theta_{\Delta\pi}-90^\circ$ ) values provide a useful index of the local strain.<sup>16</sup> The Mulliken charge densities and POAV ( $\theta_{\Delta\pi}-90^\circ$ ) values in La@C<sub>82</sub> are shown in Figure 3.<sup>10</sup> Both values are found to be large for the carbons in the six-membered ring nearest to the La atom. This suggests that one of the six electron-rich strained carbons would selectively attack **3**, since it acts as an electrophile.<sup>17</sup> The formation of **2** is uniquely different to any of the C<sub>60</sub> examples.<sup>15</sup> In fact, the addition takes place between the carbon atoms, C(1) and C(2), as indicated by the X-ray analysis results (Figure 2).

In view of the electron-acceptor and -donor character of La@C<sub>82</sub>,<sup>18</sup> there is great interest in the electrochemical behavior of the La@C<sub>82</sub> derivative bearing an organic addend. Table 1 shows the first redox potentials of adduct **2** obtained by cyclic voltammetry at room temperature. Adduct **2** exhibits three one-electron reversible reduction waves and two oxidation waves, as observed for the La@C<sub>82</sub>. The salient feature is that the redox potentials of **2** are cathodically shifted, indicating that the introduction of an Ad group results in decreasing the electron-accepting property, as confirmed by the calculated electron affinities (Ea) in Table 1.<sup>19</sup>

Our study of the highly selective derivatization of La@C<sub>82</sub> indicates that encapsulating metal is useful for controlling the reactivity and selectivity of fullerenes.

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**Supporting Information Available:** HPLC profile, MALDI-TOF mass and UV-vis-NIR spectra, and CV and DPV of **2**. Selected X-ray crystallographic data of **2** in CIF format at 90, 213, and 293 K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) Crystal data of a black needle of La@C<sub>82</sub>(Ad)·2.5(CS<sub>2</sub>): *fw* = 1448.27, 0.11 mm × 0.08 mm × 0.06 mm, monoclinic, *P*<sub>2</sub>/*n* (no. 14), *a* = 11.2997(5) Å, *b* = 21.8937(9) Å, *c* = 20.9096(9) Å,  $\beta$  = 101.3160(10)°, *V* = 5072.3(4) Å<sup>3</sup>, *Z* = 4, *D*<sub>calc</sub> = 1.896 g cm<sup>-3</sup>,  $\mu$  (Mo K $\alpha$ ) = 1.116 mm<sup>-1</sup>, Bruker SMART exposures = 30 s,  $\theta$  = 1.36–26.37°, *T* = 90 K, *R* = 0.1083, *R*<sub>1</sub> = 0.0903 for 8328 reflections (*I* > 2.0 $\sigma$ (*I*)) and 927 parameters. The maximum residual electron density is equal to 3.8 e Å<sup>-3</sup>. These relatively high *R*-values are due, at least in part, to structural disorder of some CS<sub>2</sub> solvate molecules and disorder of some La@C<sub>82</sub>(Ad) cage carbons over two sites. The full list of coordinates of the other atomic sites and the X-ray data at 213 and 293 K are also available in the Supporting Information.
- (10) Geometries were optimized using the Gaussian 03 program at the B3LYP level (ECP and (5s5p3d)/[4s4p3d] for La developed by Hay and Wadt and 6-31G\* for C and H). Pyramidalization angles were calculated using the POAV3 program.
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- (19) For the calculations of ionization potentials and electron affinities, the B3LYP optimization was followed by single-point calculations using 6-31+G\* for C and H.

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