Isolation and Characterization of Carbene Derivatives of La@C_{82}(C_s)

Takeshi Akasaka,*,† Takayoshi Kono,† Yoichiro Matsunaga,† Takatsugu Wakahara,† Tsukasa Nakahodo,† Midori O. Ishitsuka† Yutaka Maeda,‡ Takahiro Tsuchiya,† Tatsuhisa Kato,§ Michael T. H. Liu,⊥ Naomi Mizorogi,£ Zdenek Slanina,† and Shigeru Nagase*,£

Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Ibaraki 305-8577, Japan, Department of Chemistry, Tokyo Gakugei University, Tokyo 184-8501, Japan, Department of Chemistry, Josai University, Sakado, Saitama 350-0295, Japan, Department of Chemistry, University of Prince Edward Island, Charlottetown, Prince Edward Island, Canada C1A4P3, and Department of Theoretical and Computational Molecular Science, Institute for Molecular Science, Okazaki 444-8585, Japan

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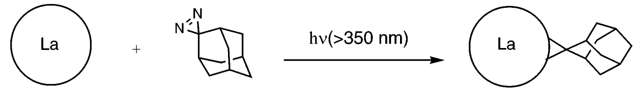
The photochemical reaction of La@C_{82}(C_s) with 2-adamantane-2,3-[3H]-diazirine (**1**) affords the adduct **2** of La@C_{82}(C_s) with adamantylidene (Ad:) in a high selectivity. The two isomers of La@C_{82}(C_s)(Ad), **2a** and **2b**, are isolated by HPLC and characterized by electron spin resonance, mass, and UV−vis−near-infrared spectroscopies. The electronic properties of **2a** and **2b** are very similar to that of the pristine La@C_{82}(C_s), suggesting that **2a** and **2b** retain the essential electronic and structural character of La@C_{82}(C_s).

1. Introduction

Endohedral metallofullerenes have attracted special attention as new spherical molecules with unique electronic properties and structures that are unexpected for empty fullerenes.[1,2] The recent successful isolation and purification of endohedral metallofullerenes have encouraged the investigation of their physical and chemical properties.[3] It is of considerable interest how the chemical reactivity and selectivity of empty fullerenes change upon endohedral metal doping.[4,5] Our earlier report indicated that the high reactivity of endohedral metallofullerenes is ascribed to their electronic properties.[5−9] It has been known that M@C_{82} (M = La, Y, Ce, Pr, etc.) is one of the most abundantly produced endohedral metallofullerenes. Among these, La@C_{82} has been recognized as a prototype of endohedral metallofullerenes since its first extraction in 1991 by Smalley and co-workers. Recently, we have verified that the major (La@C_{82}-A)[6] and minor (La@C_{82}-B)[10] isomers of La@C_{82} have C_{2v} and C_s(c) symmetry, these being hereafter abbreviated as La@C_{82}(C_{2v}) and La@C_{82}(C_s), respectively. The addition reactions of La@C_{82} can yield many regioisomers. Actually, the reactions of La@C_{82}(C_{2v}), which has 24 nonequivalent carbon atoms, with disilirane[4] and diphenyldiazomethane[11] afforded a mixture of several isomers of the monoadducts. Meanwhile, we have recently reported the first example of the regioselective reaction of La@C_{82}(C_{2v}) with 2-adamantane-2,3-[3H]-diazirine (**1**, AdN_2), in which an electrophilic adamantylidene (Ad:) attacks selectively the nucleophilic site on the C_{82}^{3-}(C_{2v}) cage to afford two isomers of the monoadduct as a major component.[12] Since La@C_{82}(C_s) has 44 nonequivalent carbon atoms, its reactions may produce a larger number of regioisomers than those of La@C_{82}(C_{2v}). Tagmatarchis et al. reported that the perfluoroalkylation of La@C_{82}(C_s) gave seven isomers of the monoadducts in a nonselective way.[13] Herein, we report for the first time a regioselective reaction of La@C_{82}(C_s).

SCHEME 1



La@C_{82}(C_s) **1** **2a** and **2b**

2. Experimental Section

Soot containing endohedral metallofullerenes was produced by the arc vaporization method using a composite anode rod containing graphite and a metal oxide.[14] The composite rod was subjected to an arc discharge as the anode in a helium atmosphere at 50 Torr. The soot was collected and suspended in 1,2,4-trichlorobenzene (TCB). After refluxing for 16 h, the TCB solution was filtered and then subjected to HPLC in order to separate La@C_{82}(C_s); a PBB column (ϕ20 mm × 250 mm; Nacalai Tesque, Inc.) and chlorobenzene as the mobile phase were used in the first step, and a Buckyprep column (ϕ20 mm × 250 mm; Nacalai Tesque, Inc.) and toluene were used in the second step.

Diazirine (**1**) was prepared according to a literature method.[15] Electrochemical-grade tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) purchased from Wako was recrystallized from ethanol and dried in a vacuum at 313 K prior to use. *o*-Dichlorobenzene (ODCB) was distilled over P_2O_5 under vacuum prior to use. The mass spectroscopic measurements were carried out using a Bruker MALDI Biflex III. The vis−near-IR absorption spectra were measured on a Shimadzu UV-3150 spectrometer in ODCB. The EPR spectra were recorded on Bruker EMX-T.

Irradiation of a TCB/toluene solution of La@C_{82}(C_s) (1 mg, 8.9×10^{-5} M) and an excess amount of AdN_2 (**1**) in a degassed

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* Authors to whom correspondence should be addressed. E-mail: akasaka@tara.tsukuba.ac.jp (T.A.); nagase@ims.ac.jp (S.N.). Phone: +81-298-53-6409 (T.A.); +81-564-55-7300 (S.N.). Fax: +81-298-53-6409 (T.A.); +81-564 53-4660 (S.N.).

† University of Tsukuba.

‡ Tokyo Gakugei University.

§ Josai University.

⊥ University of Prince Edward Island.

£ Institute for Molecular Science.

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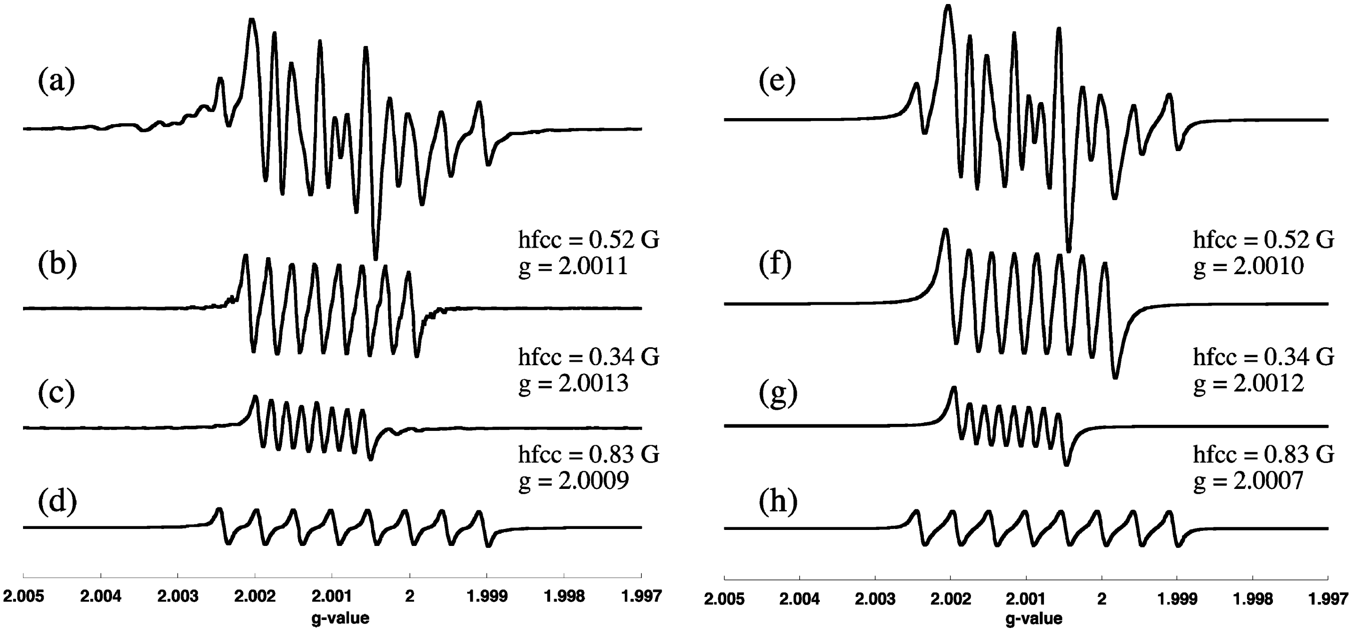


Figure 1. EPR spectra of (a) the reaction mixture, (b) **2a**, (c) **2b**, and (d) La@C$_{82}$(C_s) in toluene and the simulated EPR spectra of (e) the reaction mixture, (f) **2a**, (g) **2b**, and (h) La@C$_{82}$(C_s).

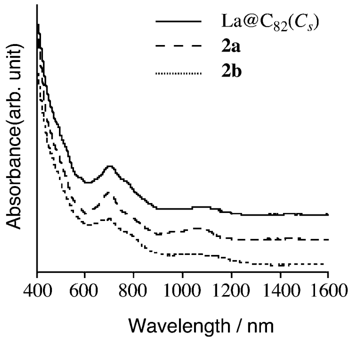


Figure 2. UV−vis−NIR spectra of La@C$_{82}$(C_s), **2a**, and **2b**.

TABLE 1: Redox Potentials (V) of La@C$_{82}$(C_s), 2a, and 2b[a]

compd	ox E_1	red E_1	red E_2
La@C$_{82}$(C_s)	−0.07	−0.54	−1.47
2a	−0.12	−0.57	−1.48
2b	−0.20	−0.60	−1.49[b]

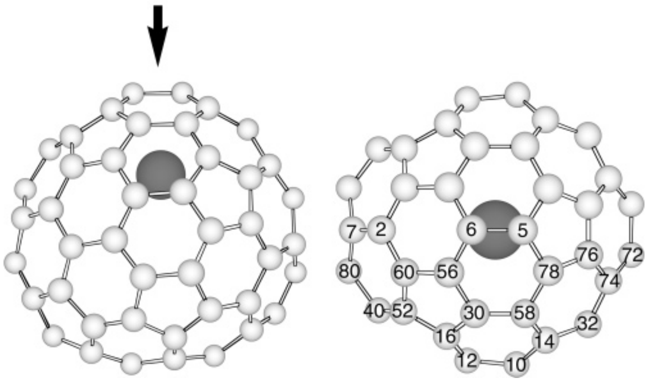
[a] In 1,2-dichlorobenzene with 0.1 M (n-Bu)$_4$NPF$_6$ at a Pt working electrode. Values were obtained by DPV: pulse amplitude, 50 mV. [b] Irreversible.

sealed tube at room temperature using a high-pressure mercury-arc lamp (cutoff <350 nm) resulted in the formation of the adducts La@C$_{82}$(C_s)(Ad) (**2a** and **2b**) (Scheme 1). On the basis of the HPLC profile, 70% of La@C$_{82}$(C_s) was consumed. A reaction mixture was subjected to HPLC to isolate the two isomers (**2a** and **2b**); a Buckyprep column (ϕ20 mm × 250 mm; Nacalai Tesque, Inc.) was used.

Theoretical calculations were performed using the Gaussian 03 program.[16] Geometries were optimized with hybrid density functional theory at the B3LYP[17−19] level. The relativistic effective core potential and the corresponding basis set[20] were used for La, and electrons in the outermost core orbitals were explicitly treated as valence electrons. For C and H, the split-valence 3-21G basis set[21a] was used for geometry optimization and the larger 6-31G* basis set[21b] for energy calculations. For La, the (5s5p3d)/[4s4p3d] contraction scheme[20a] was employed in the geometry optimizations (B3LYP/3-21G∼la), whereas for energy calculations either the B3LYP/6-31G*∼la treatment was applied or its modification with the SDD basis set[20b] on La (B3LYP/6-31G*∼sdd), both in the B3LYP/3-21G∼la optimized geometries.

TABLE 2: Selected Charge Densities and POAV Values of La@C$_{82}$(C_s) Calculated at the B3LYP/3-21G∼la Level

C	Charge density	POAV
6	-0.165	12.01
5	-0.155	11.89
56	-0.145	9.98
58	-0.136	9.47
78	-0.113	10.73
30	-0.082	10.10
76	-0.068	9.11
60	-0.048	10.16



3. Results and Discussion

A TCB/toluene solution of La@C$_{82}$(C_s) (1 mg, 8.9 × 10^{-5} M) and an excess molar amount of AdN$_2$ (**1**) was photoirradiated at room temperature with a high-pressure mercury-arc lamp (cutoff <350 nm) in a degassed sealed tube. The reaction was

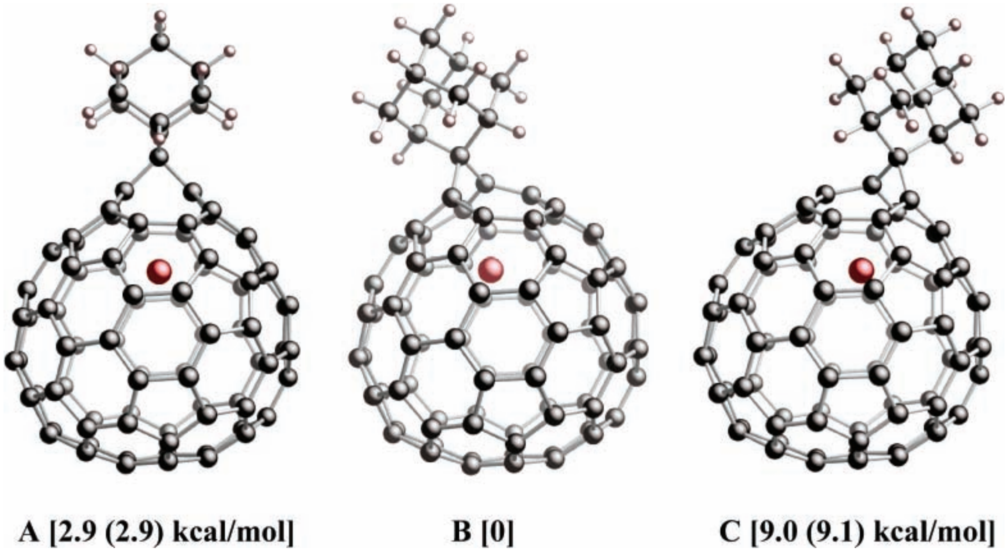


Figure 3. Optimized structures for the monoadducts of La@C_{82}(C_s)(Ad), **A**, **B**, and **C**, and their relative energies calculated at the B3LYP/6-31G*∼la//B3LYP/3-21G∼la (B3LYP/6-31G*∼sdd//B3LYP/3-21G∼la) level.

followed by the EPR measurement of the reaction mixture at different times, in which the disappearance of the octet lines for La@C_{82}(C_s) and the appearance of new two sets of octet lines were observed. Simulation of the EPR spectrum of the reaction mixture indicated the formation of two sets of octet lines in the ratio of 2 to 1 (Figure 1). The MALDI-TOF (matrix-assisted laser desorption ionization time-of-flight) mass spectrum of the reaction mixture exhibits a molecular ion peak of the monoadduct, La@C_{82}(C_s)(Ad), at m/z 1257 and a peak at m/z 1123 for La@C_{82}. The observed isotopic distribution is consistent with the calculated one, supporting the formation of the monoadduct. These results indicate that there are two isomers (**2a** and **2b**) for La@C_{82}(C_s)(Ad). **2a** and **2b** (the ratio is 4:1) were obtained in 30% yield based on the 70% consumed La@C_{82}(C_s), as monitored by HPLC, which were isolated and purified by preparative HPLC. Figure 1 shows the EPR data of **2a** and **2b**.

Recently, we reported the adamantylidene adducts of La@C_{82}(C_{2v}).[12] In view of the electron donor and acceptor character of La@C_{82}(C_s),[22] there is considerable interest in the electronic property behavior of the La@C_{82}(C_s) derivative bearing an organic addend. The UV−vis−near-infrared absorption spectra of **2a** and **2b** are similar to that of the pristine La@C_{82}(C_s) (Figure 2). Table 1 summarizes the redox potentials of La@C_{82}(C_s), **2a**, and **2b**, which were obtained by differential pulse voltammetry (DPV) at room temperature. The redox potentials of **2a** and **2b** are also very similar to those of La@C_{82}(C_s). These results suggest that **2a** and **2b** retain the essential electronic and structural character of La@C_{82}(C_s), as in the case of La@C_{82}(C_{2v})(Ad).[12]

Table 2 shows the Mulliken charge densities and the p-orbital axis vector analysis (POAV)[23] values calculated for La@C_{82}(C_s). As indicated by POAV values, carbons C5 and C6 are most highly strained. Negative charges are localized on carbons C5, C6, C56, and C78 that are close to the La atom. These suggest that it is the most favorable for the electrophilic adamantylidene[12] to react with the electron-rich C5−C6, C6−C56, and C5−C78 bonds including the locally strained C5 and C6 atoms and afford the monoadducts, **A**, **B**, and **C** (Figure 3), respectively, as found for the reaction of La@C_{82} (C_{2v}) with Ad:.[12] In order to obtain more information about the formation of **A**, **B**, and **C**, we calculated their relative energies, as shown in Figure 3. **A** and **B** are 6 and 9 kcal/mol more stable than **C**, respectively. From these results, it may be reasonable to assume that the major and minor product, **2a** and **2b**, correspond to the most stable **B** and second most stable **A** structures, respectively. The structural confirmation of **2a** and **2b** by single-crystal X-ray crystallographic analysis is in progress. Meanwhile, Nishibori et al. performed the maximum entropy method/Rietveld analysis of La@C_{82}(C_{2v}) using synchrotron powder diffraction data.[24] Their results suggest that the La cation shows temperature-dependent giant motions inside the C_{82} cage, which will affect the charge distribution of La@C_{82}(C_{2v}).[24] Very recently, Jin et al., however, have reported the much smaller motion of the La cation in La@C_{82}(C_{2v}).[25] Moreover, theoretical calculations suggest that the motions are restricted by exohedral functionalization.[26]

4. Conclusion

The derivatives of La@C_{82}(C_s), **2a** and **2b**, were successfully synthesized and characterized by the absorption and EPR spectroscopic analyses. Their electronic properties were also verified. Theoretical calculation confirms that two electron-rich bonds react with adamantylidene to afford **2a** and **2b**, leading to the regioselective addition reaction of La@C_{82}(C_s).

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Supporting Information Available: HPLC profile, LD-TOF mass and DPV of **2a** and **2b**, charge densities and POAV values of La@C_{82}(C_s), the complete lists of authors for refs 6, 12a, and 16. This material is available free of charge via the Internet at http://pubs.acs.org.

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