Chemical Reactivity of a Metallofullerene: EPR Study of Diphenylmethano-La@C_{82} Radicals

Toshiyasu Suzuki,*[,†] Yusei Maruyama, and Tatsuhisa Kato*

Institute for Molecular Science
Myodaiji, Okazaki 444, Japan

Takeshi Akasaka

Department of Chemistry, University of Tsukuba
Tsukuba, Ibaraki 305, Japan

Kaoru Kobayashi and Shigeru Nagase

Department of Chemistry, Faculty of Education
Yokohama National University, Yokohama 240, Japan

Kazunori Yamamoto, Hideyuki Funasaka, and
Takeshi Takahashi

Nuclear Fuel Technology Development Division
Tokai Works, Power Reactor and
Nuclear Fuel Development Corporation
Tokai, Ibaraki 319-11, Japan

Received March 30, 1995

The organic chemistry of fullerenes has been growing rapidly.[1] Among the variety of addition reactions to C_{60} and higher fullerenes, cycloadditions, such as dipolar additions and Diels–Alder reactions, are the most versatile ways to prepare functionalized fullerenes.[2] These reactions have been applied to produce exohedral fullerene derivatives which show intriguing physical and biochemical properties.[3,4] On the other hand, some endohedral metallofullerenes[5] have been prepared by an arc heating method and isolated by HPLC.[6–10] Theoretical[11] and electrochemical[12,13] studies have revealed that monometallofullerenes, such as La@C_{82} and Y@C_{82}, are neutral radicals which have lower ionization potentials and higher electron affinities compared to known fullerenes. Kikuchi et al. demonstrated the formation of fullerenes containing radioactive atoms inside the cages by neutron irradiation.[14] These radioactive metallofullerenes might be useful as molecular tracers for the biological and medical fields if they are functionalized. Very recently, Akasaka et al. reported photochemical and thermal additions of disilirane to La@C_{82}.[15] We now describe the first C–C bond formation on La@C_{82} and characterization of the products by EPR.

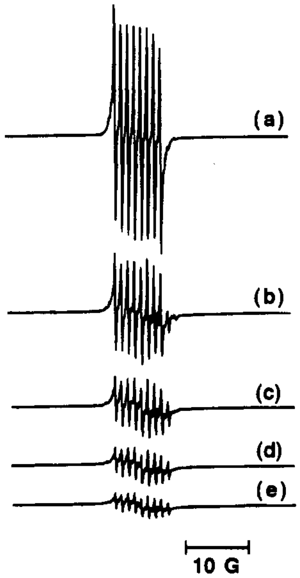

Figure 1. EPR spectra of the reaction mixture containing La@C_{82} and an excess of diphenyldiazomethane in toluene: (a) 0 min; (b) 30 min; (c) 90 min; (d) 150 min; (e) 210 min.

The production and purification of La@C_{82} were previously reported.[7] We chose diphenyldiazomethane (Ph_2CN_2) as a reactant, because methanofullerene–fulleroid chemistry has been extensively investigated by several groups.[16–19] Because it is not easy to get a large amount of pure metallofullerene, we worked with 1 mg of pure La@C_{82}. An excess of diphenyldiazomethane was added to a toluene solution of La@C_{82} in an EPR tube. The reaction was carried out at 60 °C, and the EPR spectra were recorded every 30 min at room temperature (Figure 1). The peak intensity of the octet due to La@C_{82} fell exponentially, while the intensities of the new octets increased and then decreased. Unlike the case of the disilirane adducts,[15] the new EPR signals in this case are very sharp.

We simulated the EPR spectrum at 210 min (Figure 2d) and found at least five different octets, listed in Table 1.[20] As seen in Figure 2a, this gave a satisfactory result except for the

---

[†] Present address: Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba 305, Japan.

(1) For recent reviews, see: (a) Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1138. (b) Taylor, R.; Walton, D. R. M. *Nature* **1993**, *363*, 685.

(2) Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 157.

(3) (a) Shi, S.; Khemani, K. C.; Li, Q.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 10656. (b) Rubin, Y.; Khan, S.; Freedberg, D. I.; Yeretzian, C. *J. Am. Chem. Soc.* **1993**, *115*, 344. (c) Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J.; Wudl, F.; Srdanov, G.; Shi, S.; Li, C.; Kao, M. *J. Am. Chem. Soc.* **1993**, *115*, 9836. (d) Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1993**, *115*, 10366.

(4) (a) Friedman, S. H.; DeCamp, D. L.; Sijbesma, R. P.; Srdanov, G.; Wudl, F.; Kenyon, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 6506. (b) Sijbesma, R.; Srdanov, G.; Wudl, F.; Castoro, J. A.; Wilkins, C.; Friedman, S. H.; DeCamp, D. L.; Kenyon, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 6510. (c) Tokuyama, H.; Yamago, S.; Nakamura, E.; Shiraki, T.; Sugiura, Y. *J. Am. Chem. Soc.* **1993**, *115*, 7918.

(5) For a recent review on metallofullerenes, see: Bethune, D. S.; Johnson, R. D.; Salem, J. R.; de Vries, M. S.; Yannoni, C. S. *Nature* **1993**, *366*, 123.

(6) Kikuchi, K.; Suzuki, S.; Nakao, Y.; Nakahara, N.; Wakabayashi, T.; Shiromaru, H.; Saito, K.; Ikemoto, I.; Achiba, Y. *Chem. Phys. Lett.* **1993**, *216*, 67.

(7) Yamamoto, K.; Funasaka, H.; Takahashi, T.; Akasaka, T. *J. Phys. Chem.* **1994**, *98*, 2008.

(8) (a) Shinohara, H.; Yamaguchi, H.; Hayashi, N.; Sato, H.; Ohkochi, M.; Ando, Y.; Saito, Y. *J. Phys. Chem.* **1993**, *97*, 4259. (b) Shinohara, H.; Hayashi, N.; Sato, H.; Saito, Y.; Wang, X.-D.; Hashizume, T.; Sakurai, T. *J. Phys. Chem.* **1993**, *97*, 13438.

(9) Beyers, R.; Kiang, C.-H.; Johnson, R. D.; Salem, J. R.; de Vries, M. S.; Yannoni, C. S.; Bethune, D. S.; Dorn, H. C.; Burbank, P.; Harich, K.; Stevenson, S. *Nature* **1994**, *370*, 196.

(10) Xiao, J.; Savina, M. R.; Martin, G. B.; Francis, A. H.; Meyerhoff, M. E. *J. Am. Chem. Soc.* **1994**, *116*, 9341.

(11) (a) Nagase, S.; Kobayashi, K.; Kato, T.; Achiba, Y. *Chem. Phys. Lett.* **1993**, *201*, 475. (b) Nagase, S.; Kobayashi, K. *Chem. Phys. Lett.* **1993**, *214*, 57. (c) Nagase, S.; Kobayashi, K. *J. Chem. Soc., Chem. Commun.* **1994**, 1837. (d) Nagase, S.; Kobayashi, K. *Chem. Phys. Lett.* **1994**, *228*, 106. (e) Nagase, S.; Kobayashi, K. *Chem. Phys. Lett.* **1994**, *231*, 319.

(12) Suzuki, T.; Maruyama, Y.; Kato, T.; Kikuchi, K.; Achiba, Y. *J. Am. Chem. Soc.* **1993**, *115*, 11006.

(13) Kikuchi, K.; Nakao, Y.; Suzuki, S.; Achiba, Y.; Suzuki, T.; Maruyama, Y. *J. Am. Chem. Soc.* **1994**, *116*, 9367.

(14) Kikuchi, K.; Kobayashi, K.; Sueki, K.; Suzuki, S.; Nakahara, H.; Achiba, Y.; Tomura, K.; Katada, M. *J. Am. Chem. Soc.* **1994**, *116*, 9775.

(15) Akasaka, T.; Kato, T.; Kobayashi, K.; Nagase, S.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *Nature* **1995**, *374*, 600.

(16) (a) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, Ö. *Science* **1991**, *254*, 1186–1188. (b) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301. (c) Prato, M.; Lucchini, V.; Maggini, M.; Stimpfl, E.; Scorrano, G.; Eiermann, M.; Suzuki, T.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 8479.

(17) Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; King, R. C. *J. Am. Chem. Soc.* **1993**, *115*, 5829.

(18) Diederich, F.; Issacs, L.; Philp, D. *Chem. Soc. Rev.* **1994**, 243.

(19) Hirsch, A.; Lamparth, I.; Grösser, T.; Karfunkel, H. R. *J. Am. Chem. Soc.* **1994**, *116*, 9385.

(20) It is very difficult to determine the *g* values and coupling constants for the other minor octets because their relative intensities are less than 10%.

0002-7863/95/1517-9606$09.00/0

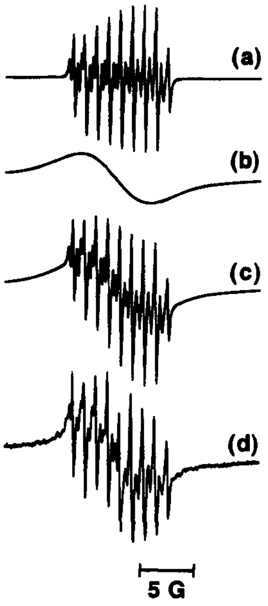

Figure 2. Experimental and simulated EPR spectra: (a) spectrum simulated with the five octets in Table 1; (b) the derivative of a Gaussian line; (c) spectrum obtained by adding Figure 2b to Figure 2a; (d) experimental spectrum at 210 min.

Table 1. EPR Parameters for La@C_{82} and Four Octet Species

octet	hyperfine coupling constant (G)	g value	rel int
La@C_{82}	1.15	2.0012	1.00
A	1.18	2.0006	0.73
B	1.17	2.0009	0.45
C	1.14	2.0015	0.31
D	1.13	2.0008	0.18

background. Then, the derivative of a Gaussian line (Figure 2b) was added to Figure 2a, affording an improved simulation as shown in Figure 2c. The salient feature in this simulation is that these new octet species (A–D in Table 1) have almost the same hyperfine coupling constants (1.13–1.18 G) and g values (2.0006–2.0015) as those of La@C_{82} (1.15 G and 2.0012).[21] This may indicate that the electronic structure of La@C_{82} is not much affected by the exohedral addition of a diphenylmethylene. In the case of the disilirane adducts,[15] the hyperfine coupling constants for the two major isomers are much larger (1.7 and 1.8 G), probably due to electron donation from the silicon atoms to the cage.[22]

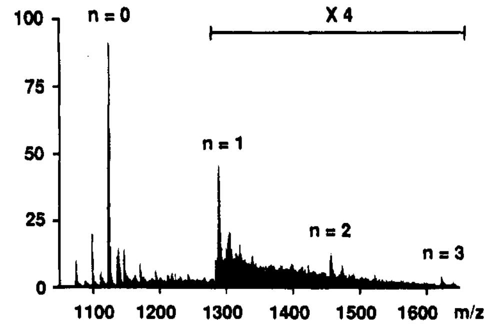

Figure 3. FAB mass spectrum of the products containing La@C_{82}-$(CPh_2)_n$ (n = 0–3).

At 220 min, the excess of diphenyldiazomethane was removed by washing with hexane. The FAB mass spectrum of the resulting precipitate shows the peaks due to La@C_{82} and mono- to trisadducts (Figure 3). The visible–near-IR absorption spectrum of the products displays broad near-IR absorption bands due to their open-shell electronic structures which are characteristic for the EPR-active monometallofullerenes.[6,7,13] At this point, however, we do not have enough information to tell the exact structures of the adducts. We speculate that (1) octets A–D are due to the monoaddition regioisomers which have the cyclopropane or annulene structures,[16–19] (2) the broad EPR signals (Figure 2b) are due to the bis- and trisadducts because there are so many possible isomers, and (3) the EPR changes correspond to the stepwise additions of diphenyldiazomethane to the C_{82} cage as observed for the reaction of C_{60} with diphenyldiazomethane (Ph_2C_{61} to $Ph_{12}C_{66}$).[16a]

In summary, we have synthesized the first methanofullerene derivatives of La@C_{82} and shown that the metallofullerene can be functionalized while retaining its unique electronic properties. We are currently applying this technology to produce water-soluble metallofullerenes.[4]

Acknowledgment. This work was supported by the Ministry of Education, Science and Culture of Japan (No. 06224230).

JA9510323

---

[21] The hyperfine coupling constants and g values of the La@C_n (n = 76, 82, 84) largely depend on the cage structures (0.44–3.15 G and 2.0002–2.0043, respectively). Bandow, S.; Kitagawa, H.; Mitani, T.; Inokuchi, H.; Saito, Y.; Yamaguchi, H.; Hayashi, N.; Sato, H.; Shinohara, H. *J. Phys. Chem.* **1992**, *96*, 9609.

[22] Suzuki, T.; Maruyama, Y.; Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, *116*, 1359.