Communication

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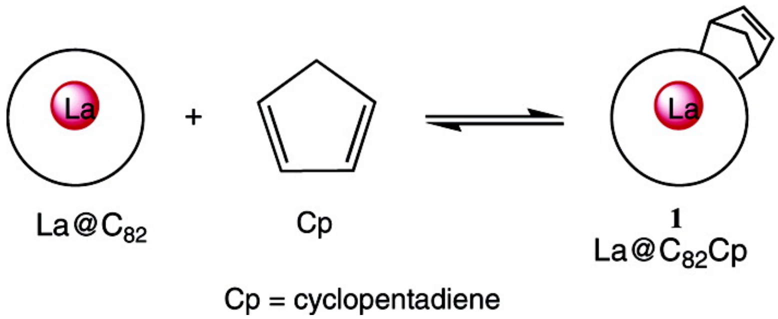

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Reversible and Regioselective Reaction of La@C$_{82}$ with Cyclopentadiene

Yutaka Maeda,[†] Jun Miyashita,[†] Tadashi Hasegawa,[*,†] Takatsugu Wakahara,[‡] Takahiro Tsuchiya,[‡]
Tsukasa Nakahodo,[‡] Takeshi Akasaka,[*,‡] Naomi Mizorogi,[§] Kaoru Kobayashi,[§] Shigeru Nagase,[*,§]
Tatsuhisa Kato,[¶] Noritaka Ban,[#] Hiroshi Nakajima,[#] and Yoshihito Watanabe[#]

Department of Chemistry, Tokyo Gakugei University, Koganei, Tokyo 184-8501, Japan, Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan, Department of Theoretical Molecular Science, Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan, Department of Chemistry, Josai University, Sakado, Saitama 350-0295, Japan, and Department of Chemistry, Graduate School of Science, Nagoya University, Nagoya, Aichi 464-8602, Japan

Received June 16, 2005; E-mail: tadashi@u-gakugei.ac.jp; akasaka@tara.tsukuba.ac.jp; nagase@ism.ac.jp

Endohedral fullerene is a new type of carbon cluster that contains one or more atoms inside the hollow fullerene cage.[1] Especially, endohedral metallofullerenes have attracted broad attention because of their novel properties due to an intramolecular metal−fullerene cage interaction. New electronic properties, such as the low oxidation and reduction potentials, induced by the interaction would allow new application of the fullerenes. Reversible addition reaction[2] is one of the useful methods for separation[3] of fullerenes and protection of their reactive site.[4] In this context, it is extremely important to develop a reversible reaction of endohedral metallofullerenes. We report here the first reversible and regioselective addition reaction of La@C$_{82}$ with cyclopentadiene (Cp).

A toluene solution of La@C$_{82}$ and Cp was placed in a quartz tube and degassed. The reaction of La@C$_{82}$ with Cp at room temperature was monitored by EPR spectroscopy. When La@C$_{82}$ and Cp were equimolecular (2.9×10^{-5} M), no change was observed in the EPR spectrum. However, when an excess of Cp (5.5×10^{-1} M) was used, a new set of octet signals appeared and their intensities increased as the La@C$_{82}$ signals decreased. After standing for 2 h in the dark, the 1:1 adduct (**1**, La@C$_{82}$Cp) between La@C$_{82}$ and Cp was isolated with HPLC in 44% yield. The electrospray ionization (ESI) mass spectrum (negative mode) of **1** showed a weak molecular ion peak at *m*/*z* 1189 for $\mathbf{1}^-$ together with a strong signal at *m*/*z* 1123 for [La@C$_{82}$]$^-$, which arises from a loss of Cp. The EPR spectrum of **1** showed only one set of octet signals and confirms that one conformer is selectively formed in the reaction of La@C$_{82}$ and Cp. As La@C$_{82}$ has C_{2v} symmetry,[5] there are 24 nonequivalent carbons and 19 nonequivalent 6,6-ring junctions. Therefore, a large number of regioisomers are expected for the monoadduct.[6] In this context, the high regioselective reaction of La@C$_{82}$ with Cp is noteworthy. As shown in Figure 1,[7] there are four characteristic bonds (2−3, 11−14, 16−19, and 15−18) that have the large orbital coefficient set in different phase. In these bonds, only the bond labeled 2−3 can afford one conformer. The carbon atom labeled 2 has a largest value of π-orbital axis vector (POAV) that is used as an index of the local strain.[8,9] On the basis of these findings, it is most likely that **1** has a structure shown in Figure 2.[7,10]

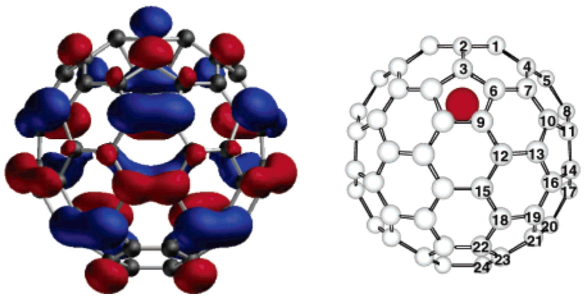


Figure 1. The LUMO of La@C$_{82}$.

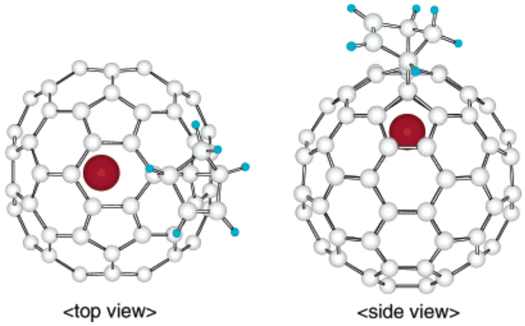
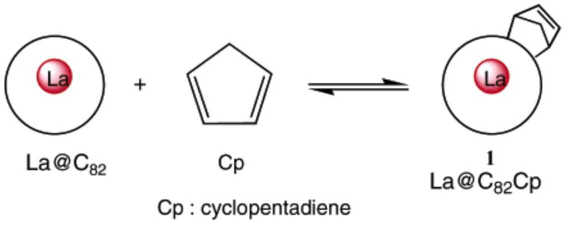


Figure 2. Two views of the optimized structure of La@C$_{82}$Cp.

Scheme 1



From the kinetic analysis, it was found that **1** decomposes to La@C$_{82}$ and Cp even at 298 K in toluene. This retro-reaction proceeds much faster than that of C$_{60}$Cp (a half-life time $\tau \sim 1.8$ h for **1** and $\tau \sim 1.8 \times 10^3$ h for C$_{60}$Cp[11]). The kinetic parameters for the retro-reactions of **1** and C$_{60}$Cp in toluene were determined at 298 K. The results are summarized in Table 1. The retro-reaction competes with the forward reaction. The activation energy for the retro-reaction of **1** was determined in the presence of maleic anhydride, which acts as a Cp scavenger and inhibits the forward reaction of La@C$_{82}$ with Cp. The activation energy was evaluated to be 100 kJ/mol. This value is 12 kJ/mol lower than that for the reaction of C$_{60}$Cp and 33−74 kJ/mol lower than those reported for retro-reactions forming normal olefins and dienes.[11−13] Since multiple adducts are unfortunately formed in the reaction of La@C$_{82}$

[†] Tokyo Gakugei University.
[‡] University of Tsukuba.
[§] Institute for Molecular Science.
[¶] Josai University.
[#] Nagoya University.

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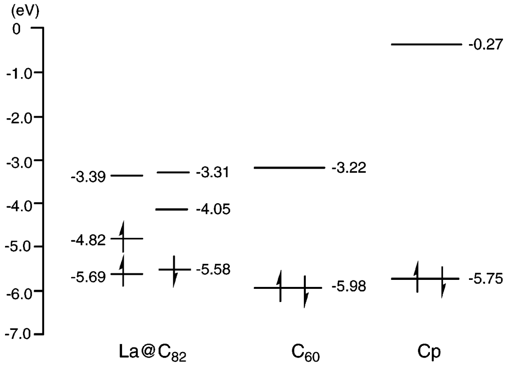

Figure 3. The orbital diagrams of La@C_{82}, C_{60}, and Cp in eV.

Table 1. The Activation and Thermodynamic (298 K) Parameters for the Retro-Reaction

	E^a (kJ/mol)	ln A	$\Delta H^‡$ (kJ/mol)	$\Delta S^‡$ (kJ/mol)	$\Delta G^‡$ (kJ/mol)
La@C_{82}Cp	100	13.6	98	7	96
C_{60}Cp[a]	112	12.6	109	−12	113

[a] Ref 11.

with Cp and the retro-reaction of **1** is fast, it is difficult to estimate the rate constants of the cycloaddition reaction.

The frontier molecular orbital (FMO) theory is useful for explaining the eletrocyclic addition. When the energy difference between the HOMO of a diene and the LUMO of an olefin is small, the cycloaddition reaction proceeds smoothly because a large stabilizing energy is formed by effective orbital interaction. From the FMO theory, La@C_{82} is expected to react with Cp faster than C_{60} because the LUMO of La@C_{82} (−4.05 eV) is lower than that of C_{60} (−3.22 eV) (Figure 3).[7] One of the reasons for the low yield of **1** would be due to the presence of the fast retro-reaction. The rate constant of consumption of La@C_{82} is 2200 times slower than that of C_{60} at 293 K.[2c]

In conclusion, we have successfully demonstrated the first reversible and regioselective reaction of La@C_{82} with Cp. The kinetic parameters for the retro-reaction of **1** (La@C_{82}Cp) were determined. Its activation energy is lower than that of the retro-reaction of C_{60}Cp. This reversible reaction would be useful to control the regioselective reactions of endohedral metallofullerenes.

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Supporting Information Available: The complete list of authors for refs 5, 6f, and 17. The HPLC profile, ESI mass spectrum, and EPR spectra of adduct **1**. The rate constants for the forward reaction of La@C_{82} with Cp and its retro-reaction. The POAV values of La@C_{82}. This material is available free of charge via the Internet at http://pubs.acs.org.

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