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Chemical Derivatization of Endohedral Metallofullerene La@C_{82} with Digermirane

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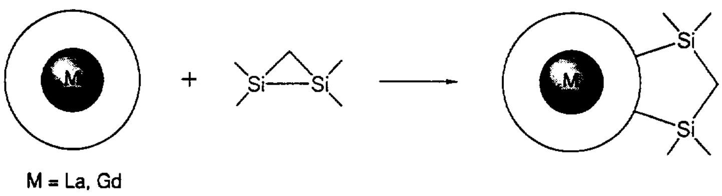
Abstract: Addition reaction of an endohedral metallofullerene La@C_{82} with digermirane has been investigated by means of the mass and EPR measurements. It is found that photochemical and thermal reactions of La@C_{82} with digermirane afford an exohedral adduct of the endohedral metallofullerene. This is in sharp contrast with the fact that empty fullerenes react only photochemically. The remarkable thermal reactivity of La@C_{82} is ascribed to the unique electronic properties due to endohedral metal doping.

INTRODUCTION

Since the first proposal[1] just after discovery[2] of C_{60} in carbon soot by Kroto, Smalley and coworkers in 1985, endohedral metallofullerenes (fullerenes with metal(s) inside the hollow spherical cage) have long attracted special interest which is motivated by the possibility that appropriate internal dopants can be used to

Scheme 1



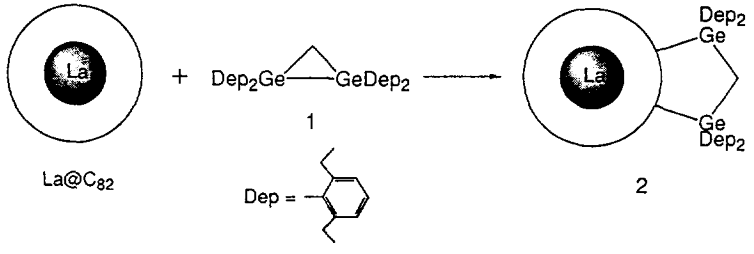
tune the physical and chemical properties, giving rise to new kinds of materials with several applications.[3] Given great efforts for the production and isolation,[3-5] group 3 atoms (Y,[6] La[7]) and Gd[8] can be trapped inside the cage of C_{82} to form a separable, soluble, and air-stable metallofullerene. Although no direct structural information is yet available for M@C_{82}, the endohedral metal trapping has been supported by the mass spectrometric, EPR spectroscopic, and fragmentation evidence. Exploration of the properties of these novel molecules should be accelerated in light of these developments. However, little is known yet about the physical property and there are no reports concerning the chemical property of these species. During the course of our studies on the chemical derivatization of fullerenes, we have found a new photochemical exohedral derivatization of typical empty fullerenes such as C_{60}[9] and C_{70}[10] with disilirane while the corresponding derivatization does not occur thermally. Moreover, we have very recently found for the first time the chemical derivatization of endohedral metallofullerenes, La@C_{82}[11] and Gd@C_{82},[12] with disilirane forming an exohedral adduct (Scheme 1). A finding is that the metallofullerenes can be exohedrally derivatized with the organosilicon compound in both thermal and photochemical ways. Since a strained Ge-Ge σ bond[13] is known to act as an electron donor, as is an Si-Si σ bond,[14] it is very interesting to investigate how the Ge-Ge σ bond reacts with La@C_{82}. Thus, we report here the photochemical and thermal reactions of La@C_{82} with digermirane in comparison with disilirane.

RESULTS AND DISCUSSION

A 1,2,4-trichlorobenzene solution of La@C_{82}[7b] (0.1mg) and 1,1,2,2-tetrakis(2,6-diethylphenyl)-1,2-digermirane [$(Dep_2Ge)_2CH_2$] (**1**, Dep=2,6-diethylphenyl)[13a] was photoirradiated at 20 °C with a tungsten-halogen lamp (cutoff<400 nm) in a degassed sealed tube (Scheme 2). The reaction product was analyzed by fast atom bombardment (FAB) mass spectrometry and EPR spectroscopy. The FAB mass spectrum of the product confirms the presence of an 1:1 adduct, La@$C_{82}(Dep_2Ge)_2CH_2$ (**2**), as shown in Figure 1. No molecular ion peak ascribable to the multiple-addition products such as La@$C_{82}[(Dep_2Ge)_2CH_2]_2$ was observed. The observed ion intensity ratio of a group of peaks at 1811-1821 for **2** agrees with the carbon and germanium isotope distributions (Figure 2). In both mass spectra, the ion peak due to La@C_{82} is a base peak. The FAB mass analyses of the disilirane adducts of metallofullerenes, La@$C_{82}(Mes_2Si)_2CH_2$[11] and Gd@$C_{82}(Mes_2Si)_2CH_2$[12] (Mes=mesityl), show strong fragmentation peaks such as La@C_{82} and Gd@C_{82}, respectively, due to loss of the exohedral functional group [$(Mes_2Si)_2CH_2$] from the adducts.

In Figure 3, the EPR spectrum of the adduct (**2**) in 1,2,4-trichlorobenzene is compared with that of La@C_{82} having one set of equally spaced octet lines with a 1.15G hyperfine splitting.[7] It should be noted

Scheme 2



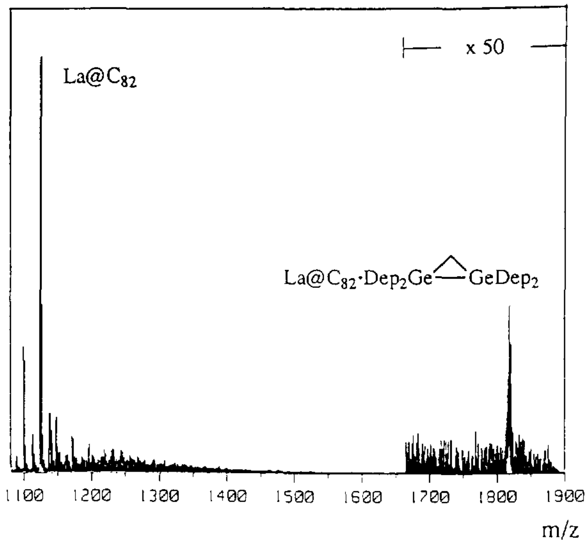


Figure 1. FAB mass spectrum of the adduct 2.

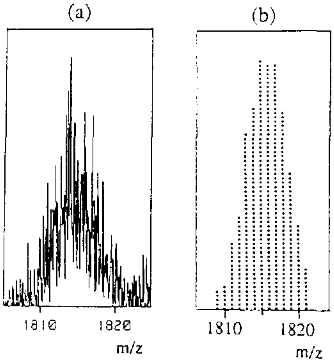


Figure 2. Mass spectra for the adduct 2: (a) Observed abundance of isotopomers of M^+ in FAB mass spectrum. (b) Its computer simulation for 2.

that the original set of octet lines of La@C_{82} is almost absent and several new sets of octet lines appear instead in the EPR spectrum of the adduct. This reveals the formation of at least three regioisomers with slightly different La isotropic splittings. The sets of octet lines observed for 2 are indicative of the conservation of the EPR-active character of La. The existence of at least three different octets is also confirmed by the simulation of the EPR spectrum after the complete consumption of La@C_{82}. An interesting finding from this simulation is that three octet species have the larger HFC constants (1.5G, 1.9G and 1.9G) than La@C_{82} (1.15G)[7] and their g values (2.0009, 2.0032 and 2.0045) are close to that of La@C_{82} (2.0012).[7] This may suggest that the exohedral addition of digermirane has a significant effect on the electronic structure of La@C_{82}. As suggested previously for the disilirane adduct (1.7-1.8G),[11] the larger HFC constants for the three isomers are probably due to electron donation from the germanium atoms to the cage. The electronic structure of La@C_{82} is formally describable as $La^{3+}C_{82}^{3-}$ as a result of the transfer of three valence electrons on La to the LUMO and

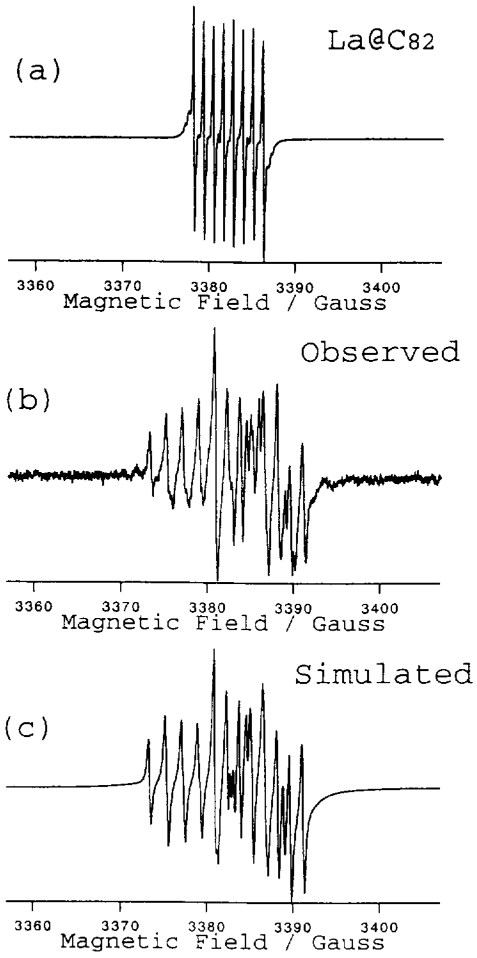


Figure 3. (a) EPR spectrum of La@C_{82}. (b) EPR spectrum of the adduct **2**. (c) Simulated EPR spectrum of the adduct **2**.

LUMO+1 of C_{82}.[15] Relatively large HFC constants of **2** compared to that of La@C_{82} suggest that the La atom is less positively charged in **2** than in La@C_{82}. It has been shown that silicon-substituents donate almost one electron into fullerene cages which consequently become electron rich, raising the LUMO and LUMO+1 levels by ca. 0.5 eV.[16] Since the electronegativities of germanium and silicon are similar,[17] the degree of electron transfer from La to the germanium-substituted fullerene cage is significantly suppressed, as found for the silicon case.[11] This is well consistent with the fact that both $C_{60}(Mes_2Si)_2CH_2$[16] and $C_{60}(Dep_2Ge)_2CH_2$[18] have similar redox potentials.

From the mass spectrometry and EPR spectroscopy, it is certain that the adduct La@$C_{82}(Dep_2Ge)_2CH_2$ is formed by the photochemical reaction of La@C_{82} with digermirane **1**, similar to the disilirane case. These successful exohedral derivatizations of endohedral metallofullerenes should trigger much more work for the preparation of functionalized metallofullerenes.

A remarkable feature of the chemical reactivity of La@C_{82} toward **1** was revealed as compared with those of typical empty fullerenes such as C_{60} and C_{70}. Although the addition of **1** onto the empty fullerenes takes place only photochemically,[18] La@C_{82} was also thermally reactive toward **1**. When a 1,2,4-trichlorobenzene solution of La@C_{82} and **1** was heated at 80 °C under dark, formation of **2** was verified by means of the FAB mass and EPR measurement. The high thermal reactivity of La@C_{82} toward **1** is explained by means of its characteristic electronic properties; i.e., stronger electron donor and acceptor character.[19] The *ab initio* molecular orbital calculation predicts that the ionization potential (6.19 eV) and electron affinity (3.22 eV) of La@C_{82} are much smaller and larger than those for C_{60} (7.78 and 2.57 eV) and C_{70}(7.64 and 2.69 eV), respectively.[19] This is well consistent with the fact that La@C_{82} has lower oxidation and reduction potentials than C_{60} and C_{70}.[20]

A finding is that even when the reaction temperature went down from 80 to 20 °C, the thermal addition of **1** onto La@C_{82} was observed, unlike the disilirane case. This is accounted for by the fact that **1** has a lower oxidation potential (0.72 V vs. SCE)[21] than 1,1,2,2-tetramesityl-1,2-disilirane (0.81 V).[22]

It should be noted that the present derivatizations differ significantly from those of endohedral novel gas fullerenes such as He@C_{60} and He@C_{70} (which allow the trapped atom to penetrate through the fullerene cage).[23] In the chemical derivatizations of La@C_{82}, the degree of the electron transfer from the electropositive metal to the fullerene cage plays a crucial role in modifying the electronic properties of the fullerene cage, unlike the novel gas case.

In conclusion, the present success in the chemical derivatizations of endohedral metallofullerenes will constitute a stepping stone on the way to a new stage for the endohedral metallofullerene chemistry. It is expected that the derivatives of endohedral metallofullerenes serve as important molecules in several fields, since they have novel properties unexpected for empty fullerenes.

EXPERIMENTAL

The production and purification of an EPR-active metallofullerene La@C_{82} were achieved with our recently developed method.[7b] A 1,2,4-trichlorobenzene solution of La@C_{82} (10^{-4} M) and an excess of 1,1,2,2-tetrakis(2,6-diethylphenyl)-1,2-digermirane [$(Dep_2Ge)_2CH_2$] (**1**)[13a] was photoirradiated at 20 °C with a tungsten-halogen lamp (cutoff<400 nm) in a degassed sealed tube or heated at 80 °C under dark. The products for both photochemical and thermal reaction were measured by the EPR and Mass spectrometers. The positive ion FAB mass spectra of the products were measured on a JEOL SX-102A mass spectrometer using *m*-nitrobenzyl alcohol as matrix. The EPR spectra were obtained with a Bruker ESR 300E Spectrometer, and the samples in 1,2,4-trichlorobenzene were degassed several times by a freeze-thaw cycle and sealed in a thin-wall quartz tube. The EPR measurement was performed at ambient temperature.

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