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Tetrahedron Letters 44 (2003) 8199–8201

TETRAHEDRON
LETTERS

Mechanochemical synthesis of a novel C_{60} dimer connected by a germanium bridge and a single bond

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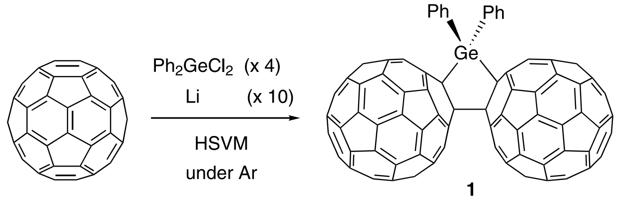
Received 9 August 2003; revised 11 September 2003; accepted 12 September 2003

Abstract—A novel C_{60} dimer connected by a germanium bridge and a single bond was synthesized by the mechanochemical solid-state reaction using a high-speed vibration milling technique. The structural characterization was made by the ^1H and ^{13}C NMR, APCI mass, and UV-vis spectroscopy, and the presence of the electronic interaction between the two C_{60} cages was demonstrated by the electrochemical method.

We have previously found that the mechanochemical solid-state reaction using the high-speed vibration milling (HSVM) technique[1] is particularly effective for the dimerization of fullerene as exemplified by the synthesis of the C_{60} dimer, C_{120},[1,2] and the C_{60}/C_{70} cross-dimer, C_{130}.[3] In these dimers, the two fullerene cages are connected by sharing a cyclobutane ring. On the other hand, there were only two reports on the C_{60} dimer connected by sharing a five-membered ring, i.e. $C_{120}X$; $X = O$[4,5] and CH_2.[4] Recently we have successfully synthesized the third example of such C_{60} dimer, $C_{120}SiPh_2$, connected by a silicon bridge and a single bond using the HSVM method.[6] The electrochemical study has revealed the presence of electronic interaction between the two C_{60} cages as well as tendency of redox potentials to shift to cathodic direction. We were interested in introducing another group 14 element such as germanium or tin into the central five-membered ring in order to examine its electronic effect upon the properties of fullerene cages. Germanium species such as cyclotetragermane,[7] germyllithium,[8] and digermirane[9] have been reported to react with fullerene C_{60} to give the mono- or di-germyl derivatives of C_{60}. Here we report the synthesis of the first example of the C_{60} dimer fused with a germacyclopentane ring (**1**) by the use of the solid-state reaction of C_{60} with dichlorodiphenylgermane and lithium metal.

A mixture of fullerene C_{60}, dichlorodiphenylgermane, and lithium powder, in a molar ratio of 1:4:10, was placed in a vibration-milling capsule together with a mixing ball under argon, and the mixture was vigorously vibrated at the rate of 3500 rpm for 30 min. The separation of the product using a Cosmosil '5PBB' column eluted with *o*-dichlorobenzene (ODCB) afforded dimer **1** in 9% isolated yield as a brown powder, while 37% of C_{60} was recovered unchanged (Scheme 1).

We suppose that the mechanism for the formation of **1** would involve the ionic reaction between dichlorodiphenylgermane and C_{60} radical anion formed by one-electron transfer from Li[10] followed by radical coupling of the two C_{60} cages. Although the similar reaction was expected for Ph_2CCl_2 or Ph_2SnCl_2 instead of Ph_2GeCl_2, the reaction using Ph_2CCl_2 gave monomeric adduct $C_{60}CPh_2$[11] in 24% isolated yield, whereas the reaction using Ph_2SnCl_2 afforded $C_{60}H_2$[12] as a major product, without the formation of corresponding dimeric species.



Scheme 1.

Keywords: fullerene C_{60}; germanium; solid-state reaction; high-speed vibration milling.

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doi:10.1016/j.tetlet.2003.09.077

The structure of **1** was determined by MS, ^{1}H and ^{13}C NMR, and UV-vis spectroscopy.[13] In the negative-ion mode atmospheric-pressure chemical ionization (APCI) MS spectrum, a molecular-ion peak at m/z 1668 corresponding to the molecular formula of $C_{132}H_{10}Ge$ was observed. The ^{1}H NMR (400 MHz, CS_2-CD_2Cl_2 (3:1)) exhibited signals at δ 8.28 (m), 7.47 (m), and 7.46 (d) ppm for *meta*-, *para*-, and *ortho*-protons, respectively. The ^{13}C NMR (100 MHz, CS_2-CD_2Cl_2 (3:1)) demonstrated 30 signals (4C×28 and 2C×2) for the sp^2 carbons of the C_{60} cage at the range from 158.10 to 134.23 ppm in addition to two signals (86.52 and 66.29 ppm) for the sp^3 carbons. The signal at δ 66.29 ppm was assigned to the sp^3 carbon directly connected to the germanium atom, which is in the range of the reported values for monomeric derivatives (δ 69–64 ppm).[7–9] These spectral data are in good agreement with the structure **1** having the C_{2v} symmetry. The ^{13}C NMR signals of the benzene-ring carbons were observed as four signals at 139.13, 132.19, 130.75, and 129.36 ppm. These results indicate that the structure of **1** consists of a germacyclopentane ring fused with two C_{60} cages at the 6–6 bonds.

In the UV-vis spectrum shown in Figure 1, two absorptions around 400 nm were observed as shoulders at 420 and 445 nm, which are similar to the absorptions of the silicon analogue (418 and 440 nm).[6]

This new dimer **1** is stable as a solid but was found to be sensitive to moisture in solution and to be transformed into C_{60} and $C_{60}H_2$ after standing for a few days in a solution containing a trace of water, as was observed for the silicon analogue of **1**.[6] The precise mechanism for this decomposition is not clear for the moment, but the strain around the germanium atom and also the presence of the germanium atom at the allylic position on the C_{60} cage in **1** would be the reasons for such a cleavage. In support of such a ready cleavage of the allylic carbon-germanium bond by water, the theoretical calculations at the B3LYP/3-21G level of theory indicated that coefficients of the HOMO are rather localized at the 'allylic' double bonds (Fig. 2) along with the 'e_{edge}' positions,[14] as was also seen in the silicon analogue of **1**. The C(sp^3)-Ge-C(sp^3) angle of dimer **1** was calculated to be 95.3°, which was distorted from the ideal C-Ge-C angle, 109.5°. The calculations also indicated that the HOMO of **1** (−6.007 eV) is almost at the same level as that of the silicon analogue (−6.015 eV) at the same level of theory.

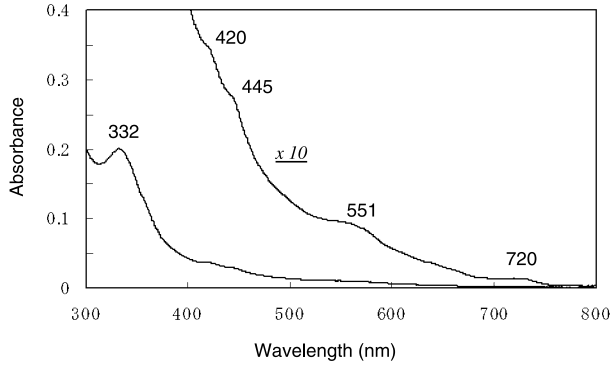

Figure 1. UV-vis spectrum of **1** in ODCB ($c=2.1\times10^{-5}$ M).

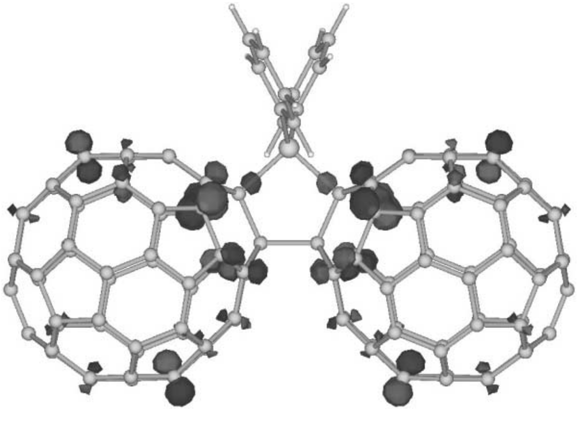

Figure 2. Molecular structure of **1** calculated at the B3LYP/3-21G level including pictorial representation of the HOMO.

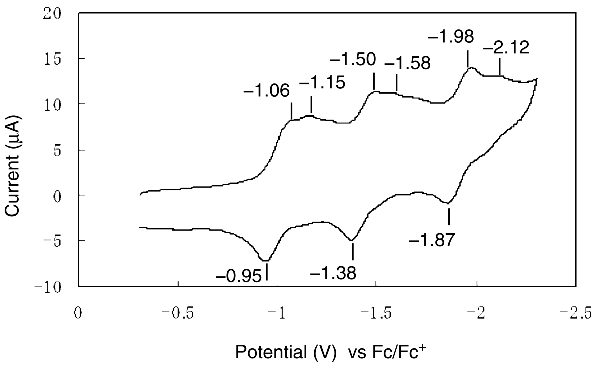

Figure 3. Cyclic voltammogram of **1** in ODCB-benzonitrile (1:1) ($c=6.4\times10^{-4}$ M) with 0.05 M Bu_4NBF_4 as a supporting elctrilyte; scan rate, 0.05 V s^{-1}.

In the case of the oxygen- and silicon-bridged C_{60} dimer, $C_{120}O$ and $C_{120}SiPh_2$, electrochemical studies indicated that there are electronic communications between the two C_{60} cages and they are reduced stepwise at slightly different potentials.[6,15] In a similar manner, the cyclic voltammetry on dimer **1** indicated that the two C_{60} cages in **1** were reduced stepwise as shown in Figure 3 at E_{pc} −1.06, −1.15, −1.50, −1.58, −1.98 and −2.12 V versus Fc/Fc^+, indicating the presence of an electronic interaction between the two C_{60} cages upon the electrochemical reduction.[16] The corresponding reduction peaks for C_{60} were observed at E_{pc} −0.97, −1.40, and −1.88 V under the same conditions. The observed general tendency of the reduction peaks to shift in a cathodic direction is attributed to the electronic effect of the germanium atom directly attached to the C_{60} cages.[9,17] Thus, introduction of germanium into the central five-membered ring results in the similar effect to silicon on the reduction potential.[6] This result is in good agreement with the calculations at the B3LYP/3-21G level of theory that the LUMO of **1** (−3.529 eV) is almost at the same level as that of the silicon analogue (−3.524 eV), and is higher than that of C_{60} (−3.568 eV).

In summary, we have expanded the realms of solid-state reactions of C_{60} using the HSVM technique to the synthesis of the organogermanium compound. A novel C_{60} dimer **1** connected by a germanium bridge and a single bond was obtained for the first time, which showed the electronic communications between two C_{60} cages upon reduction in solution.

Acknowledgements

This work was supported by a Grant-in-Aid for COE Research on Elements Science (No. 12CE2005) form the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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