JOC *Article*

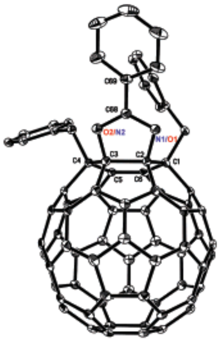
Synthesis and Identification of Heterocyclic Derivatives of Fullerene C_{60}: Unexpected Reaction of Anionic C_{60} with Benzonitrile

Min Zheng, Fang-fang Li, Ling Ni, Wei-wei Yang, and Xiang Gao*

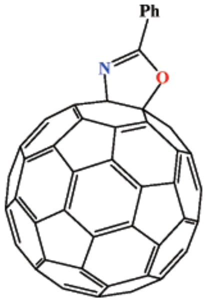
State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Graduate School of Chinese Academy of Sciences, Chinese Academy of Sciences, Changchun, Jilin 130022, China

xgao@ciac.jl.cn

Received December 17, 2007



Compound **1**



Compound **2**

During the reaction of reduced C_{60} with benzyl bromide in benzonitrile, a novel *cis*-1 C_{60} adduct, 1,4-dibenzyl-2,3-cyclic phenylimidate C_{60} (**1**), was obtained rather than the expected product of 1,4-dibenzyl C_{60}. The structure of compound **1** was analyzed by X-ray single-crystal diffraction, identifying the presence of a five-membered heterocycle at a [5,6] bond of C_{60}. One of the heteroatoms is assigned as a nitrogen atom; however, the identity of the other heteroatom cannot be determined unambiguously by crystallography due to similarity between the nitrogen and oxygen atoms. A related compound (**2**) bearing the same heterocycle was obtained from anionic C_{60} benzonitrile solution when no benzyl bromide was added. The structure of compound **2** was determined by NMR, MALDI FT-ICR MS, and UV−vis. Results from MALDI FT-ICR MS for compound **2** show unambiguously that the second heteroatom is an oxygen atom, which is probably from traces of water in the solvent. Control experiments of the reactivity of the neutral, monoanionic, dianionic, and trianionic C_{60} have shown that the reactive species for the unexpected reaction is the C_{60} trianion.

Introduction

The chemistry of fullerenes has developed dramatically[1] since a method for macroscopic production of fullerenes was reported.[2] The unique electronic and three-dimensional structure of fullerenes has enabled organic chemists to discover an astonishing variety of unprecedented reactions and functionalized regioisomers which have shown remarkable potential in areas such as organic electronics,[3] biological and medicinal chemistry,[4] materials chemistry,[5] and catalytic reagent chemistry.[6] C_{60}, the most abundant member in the fullerene family, has received the majority of synthetic attention due to its availability. It is now well-established that C_{60} is electron-deficient and reactive toward nucleophiles.[1] It has been shown that the reactions of C_{60} mainly involve the cleavage of double bonds at the [6,6] site and lead to the formation of 1,2- or 1,4-adducts depending on the size of addends.[1] Occasionally, derivatives with [5,6] open structure (fulleroids) involving the cleavage of a [5,6] single bond are also observed.[7]

The chemistry of fullerene anions has also attracted great attention since, unlike neutral fullerenes, they are electron-rich and reactive toward electrophiles.[1e,8] Due to the strong electron-

---

(1) (a) Taylor, R.; Walton, D. R. M. *Nature* **1993**, *363*, 685−693. (b) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317−324. (c) Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519−526. (d) Hirsch, A. *Top. Curr. Chem.* **1999**, *199*, 1−65. (e) Hirsch, A.; Brettreich, M. *Fullerenes: Chemistry and Reactions*; Wiley-VCH: Weinheim, Germany, 2005. (f) Martín, N. *Chem. Commun.* **2006**, 2093−2104.

(2) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354−358.

10.1021/jo702678c CCC: $40.75 © 2008 American Chemical Society
Published on Web 03/15/2008

accepting ability of the molecule,[9] C_{60} anions are readily generated by either chemical[8b,e,f,h,k−m,10] or electrochemical[8a,c,d,g,i,j,n,11] reductive methods. Previous work has shown that anionic C_{60} exhibits a different reactivity to neutral C_{60}. For example, it has been shown that organofullerenes can be obtained from neutral C_{60} by cyclopropanation reaction,[1e,12,13] while anions of organofullerenes can undergo retro-cyclopropanation reactions to selectively remove the addends.[14,15] The monoanionic C_{60} has demonstrated a better ability to complex with cyclodextrins, forming water-soluble supramolecular structures and constructing interfacial supramolecular self-assembled monolayers on a gold surface.[16] The dianionic C_{60} is also capable of preparing multiple C_{60} adducts not accessible from neutral C_{60}.[8i] In addition, it has been shown that the anions of C_{60} are excellent electron transfer mediators for reaction initiation[8e,f] and electrocatalytic reductive reactions.[17] However, studies on the reactivity of C_{60} anions are mostly limited to the reactions of C_{60}^{2-} with organic halides.[8] Much less work has appeared on the reactivity of C_{60}^{3-}, and no apparent difference has been recorded for the reactivity between C_{60}^{2-} and C_{60}^{3-} except that

---

(3) (a) Kim, Y.; Cook, S.; Tuladhar, S. M.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; Mcculloch, I.; Ha, C.-S.; Ree, M. *Nat. Mater.* **2006**, *5*, 197−203. (b) Hasobe, T.; Kamat, P. V.; Troiani, V.; Solladie, N.; Ahn, T. K.; Kim, S. K.; Kim, D.; Kongkanand, A.; Kuwabata, S.; Fukuzumi, S. *J. Phys. Chem. B* **2005**, *109*, 19−23. (c) Konishi, T.; Ikeda, A.; Shinkai, S. *Tetrahedron* **2005**, *61*, 4881−4899. (d) Kim, K.-S.; Kang, M.-S.; Ma, H.; Jen, A. K.-Y. *Chem. Mater.* **2004**, *16*, 5058−5062. (e) Ikeda, A.; Hatano, T.; Shinkai, S.; Akiyama, T.; Yamada, S. *J. Am. Chem. Soc.* **2001**, *123*, 4855−4856. (f) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789−1791. (g) Sariciftci, N. S.; Heeger, A. J. *Int. J. Mod. Phys. B* **1994**, *8*, 237−274. (h) Boutorine, A. S.; Tokuyama, H.; Takasugi, M.; Isobe, H.; Nakamura, E.; Hélène, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *33*, 2462−2465. (i) Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. M. T.; Ramirez, A. P.; Kortan, A. R. *Nature* **1991**, *350*, 600−601. (j) Holczer, K.; Klein, O.; Huang, S.-M.; Kaner, R. B.; Fu, K.-J.; Whetten, R. L.; Diederich, F. *Science* **1991**, *252*, 1154−1157. (k) Herance, J. R.; Peris, E.; Vidal, J.; Bourdelande, J. L.; Marquet, J.; García, H. *Chem. Mater.* **2005**, *17*, 4097−4102. (l) Hoshi, H.; Yamada, T.; Ishikawa, K.; Takezoe, H.; Fukuda, A. *Phys. Rev. B* **1995**, *52*, 12355−12365. (m) Martín, N.; Sánchez, L.; Illescas, B.; Pérez, I. *Chem. Rev.* **1998**, *98*, 2527−2547. (n) Lin, J.; Zheng, M.; Chen, J.; Gao, X.; Ma, D. *Inorg. Chem.* **2007**, *46*, 341−344.

(4) (a) Friedman, S. H.; DeCamp, D. L.; Sijbesma, R. P.; Srdanov, G.; Wudl, F.; Kenyon, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 6506−6509. (b) Nakamura, E.; Isobe, H. *Acc. Chem. Res.* **2003**, *36*, 807−815. (c) Gharbi, N.; Pressac, M.; Hadchouel, M.; Szwarc, H.; Wilson, S. R.; Moussa, F. *Nano Lett.* **2005**, *5*, 2578−2585. (d) Zakharian, T. Y.; Seryshev, A.; Sitharaman, B.; Gilbert, B. E.; Knight, V.; Wilson, L. J. *J. Am. Chem. Soc.* **2005**, *127*, 12508−12509. (e) Tagmatarchis, N.; Shinohara, H. *Mini-Rev. Med. Chem.* **2001**, *1*, 339−348. (f) Jensen, A. W.; Wilson, S. R.; Schuster, D. I. *Bioorg. Med. Chem.* **1996**, *4*, 767−779. (g) Da Ros, T.; Spalluto, G.; Prato, M. *Croat. Chem. Acta* **2001**, *74*, 743−755.

(5) (a) Tagmatarchis, N.; Prato, M. *Struct. Bonding* **2004**, *109*, 1−39. (b) Prato, M. *J. Mater. Chem.* **1997**, *7*, 1097−1109. (c) Wudl, F. *J. Mater. Chem.* **2002**, *12*, 1959−1963. (d) Cravino, A.; Sariciftci, N. S. *J. Mater. Chem.* **2002**, *12*, 1931−1943. (e) Yamada, H.; Imahori, H.; Fukuzumi, S. *J. Mater. Chem.* **2002**, *12*, 2034−2040. (f) Brusatin, G.; Signorini, R. *J. Mater. Chem.* **2002**, *12*, 1964−1977. (g) Guldi, D. M.; Martín, N. *J. Mater. Chem.* **2002**, *12*, 1978−1992. (h) Murata, Y.; Ito, M.; Komatsu, K. *J. Mater. Chem.* **2002**, *12*, 2009−2020. (i) Barazzouk, S.; Hotchandani, S.; Kamat, P. V. *J. Mater. Chem.* **2002**, *12*, 2021−2025. (j) Guldi, D. M.; Zerbetto, F.; Georgakilas, V.; Prato, M. *Acc. Chem. Res.* **2005**, *38*, 38−43. (k) Hasobe, T.; Imahori, H.; Kamat, P. V.; Ahn, T. K.; Kim, S. K.; Kim, D.; Fujimoto, A.; Hirakawa, T.; Fukuzumi, S. *J. Am. Chem. Soc.* **2005**, *127*, 1216−1228.

(6) (a) Nishibayashi, Y.; Saito, M.; Uemura, S.; Takekuma, S.; Takekuma, H.; Yoshida, Z. *Nature* **2004**, *428*, 279−280. (b) Takekuma, S.; Takekuma, H.; Yoshida, Z. *Chem. Commun.* **2005**, 1628−1630. (c) Pospíšil, L.; Bulíčková, J.; Hromadová, M.; Gál, M.; Ciciš, S.; Cihelka, J.; Tarábek, J. *Chem. Commun.* **2007**, *22*, 2270−2272.

(7) (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*, 7301−7302. (c) Prato, M.; Li, O.; Wudl, F.; Lucchini, V. *J. Am. Chem. Soc.* **1993**, *115*, 1148−1150. (d) Hawker, C. J.; Saville, P. M.; White, J. W. *J. Org. Chem.* **1994**, *59*, 3503−3505. (e) Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; Goldschmidt, R. J.; King, R. C. *J. Am. Chem. Soc.* **1995**, *117*, 5492−5502. (f) Hummelen, J. C.; Knight, B. W.; LePeq, F.; Wudl, F.; Yao, J.; Wilkins, C. L. *J. Org. Chem.* **1995**, *60*, 532−538. (g) Schick, G.; Grösser, T.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2289−2290. (h) Ikeda, A.; Fukuhara, C.; Shinkai, S. *Tetrahedron Lett.* **1996**, *37*, 7091−7094. (i) Zhu, C.-C.; Xu, Y.; Liu, Y.-Q.; Zhu, D.-B. *J. Org. Chem.* **1997**, *62*, 1996−2000. (j) Schick, G.; Hirsch, A. *Tetrahedron* **1998**, *54*, 4283−4296. (k) Weisman, R. B.; Heymann, D.; Bachilo, S. M. *J. Am. Chem. Soc.* **2001**, *123*, 9720−9721. (l) Ulmer, L.; Mattay, J. *Eur. J. Org. Chem.* **2003**, 2933−2940.

(8) (a) Caron, C.; Subramanian, R.; D'Souza, F.; Kim, J.; Kunter, W.; Jones, M. T.; Kadish, K. M. *J. Am. Chem. Soc.* **1993**, *115*, 8505−8506. (b) Chen, J.; Cai, R.-F.; Huang, Z.-E.; Wu, H.-M.; Jiang, S.-K.; Shao, Q.-F. *J. Chem. Soc., Chem. Commun.* **1995**, 1553−1554. (c) Boulas, P. L.; Zuo, Y.; Echegoyen, L. *Chem. Commun.* **1996**, 1547−1548. (d) Mangold, K.-M.; Kunter, W.; Dunsch, L.; Fröhner, J. *Synth. Met.* **1996**, *77*, 73−76. (e) Subramanian, R.; Kadish, K. M.; Vijayashree, M. N.; Gao, X.; Jones, M. T.; Miller, D. M.; Krause, K.; Suenobu, T.; Fukuzumi, S. *J. Phys. Chem.* **1996**, *100*, 16327−16335. (f) Fukuzumi, S.; Suenobu, T.; Hirasaka, T.; Arakawa, R.; Kadish, K. M. *J. Am. Chem. Soc.* **1998**, *120*, 9220−9227. (g) Kadish, K. M.; Gao, X.; Van Caemelbecke, E.; Hirasaka, T.; Suenobu, T.; Fukuzumi, S. *J. Phys. Chem. A* **1998**, *102*, 3898−3906. (h) Allard, E.; Rivière, L.; Delaunay, J.; Dubois, D.; Cousseau, J. *Tetrahedron Lett.* **1999**, *40*, 7223−7226. (i) Kadish, K. M.; Gao, X.; Van Caemelbecke, E.; Suenobu, T.; Fukuzumi, S. *J. Am. Chem. Soc.* **2000**, *122*, 563−570. (j) Kadish, K. M.; Gao, X.; Van Caemelbecke, E.; Suenobu, T.; Fukuzumi, S. *J. Phys. Chem. A* **2000**, *104*, 3878−3883. (k) Allard, E.; Delaunay, J.; Cheng, F.; Cousseau, J.; Orduna, J.; Garin, J. *Org. Lett.* **2001**, *3*, 3503−3506. (l) Cheng, F.; Murata, Y.; Komatsu, K. *Org. Lett.* **2002**, *4*, 2541−2544. (m) Meier, M. S.; Bergosh, R. G.; Gallagher, M. E.; Spielmann, H. P.; Wang, Z. *J. Org. Chem.* **2002**, *67*, 5946−5952. (n) Zheng, M.; Li, F.; Shi, Z.; Gao, X.; Kadish, K. M. *J. Org. Chem.* **2007**, *72*, 2538−2542.

(9) (a) Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978−3980. (b) Echegoyen, L.; Echegoyen, L. E. *Acc. Chem. Res.* **1998**, *31*, 593−601. (c) Reed, C. A.; Bolskar, R. D. *Chem. Rev.* **2000**, *100*, 1075−1120.

(10) (a) Subramanian, R.; Boulas, P.; Vijayashree, M. N.; D'Souza, F.; Jones, M. T.; Kadish, K. M. *J. Chem. Soc., Chem. Commun.* **1994**, 1847−1848. (b) Wei, X.-W.; Wu, M.-F.; Qi, L.; Xu, Z. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1389−1393.

(11) (a) Lawson, D. R.; Feldheim, D. L.; Foss, C. A.; Dorhout, P. K.; Elliott, C. M.; Martin, C. R.; Parkinson, B. *J. Electrochem. Soc.* **1992**, *139*, L68−L71. (b) Khaled, M. M.; Carlin, R. T.; Trulove, P. C.; Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1994**, *116*, 3465−3474. (c) Dubois, D.; Jones, M. T.; Kadish, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 6446−6451. (d) Stinchcombe, J.; Pénicaud, A.; Bhyrappa, P.; Boyd, P. D. W.; Reed, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 5212−5217. (e) Rapta, P.; Bartl, A.; Gromov, A.; Staško, A.; Dunsch, L. *Chem. Phys. Chem.* **2002**, *3*, 351−356. (f) Dunch, L.; Rapta, P.; Gromov, A.; Staško, A. *J. Electroanal. Chem.* **2003**, *547*, 35−43.

(12) (a) Bingel, C. *Chem. Ber.* **1993**, *126*, 1957−1959. (b) Diederich, F.; Isaacs, L.; Philp, D. *Chem. Soc. Rev.* **1994**, 243−255.

(13) (a) Eiermann, M.; Haddon, R. C.; Knight, B.; Chan Li, Q.; Maggini, M.; Martín, N.; Ohno, T.; Prato, M.; Suzuki, T.; Wudl, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1591−1593. (b) Ohno, T.; Martín, N.; Knight, B.; Wudl, F.; Suzuki, T.; Yu, H. *J. Org. Chem.* **1996**, *61*, 1306−1309. (c) Knight, B.; Martín, N.; Ohno, T.; Ortí, E.; Rovira, C.; Veciana, J.; Vidal-Gancedo, J.; Viruela, P.; Viruela, R.; Wudl, F. *J. Am. Chem. Soc.* **1997**, *109*, 9871−9882. (d) Martín, N.; Sánchez, L.; Illescas, B.; Pérez, I. *Chem. Rev.* **1998**, *98*, 2527−2547. (e) Beulen, M. W. J.; Echegoyen, L.; Rivera, J. A.; Herranz, M. A.; Martín-Domenech, A.; Martín, N. *Chem. Commun.* **2000**, 917−918.

(14) (a) Knight, B.; Martín, N.; Ohno, T.; Ortí, E.; Rovira, C.; Veciana, J.; Vidal-Gancedo, J.; Viruela, P.; Viruela, R.; Wudl, F. *J. Am. Chem. Soc.* **1997**, *119*, 9871−9882. (b) Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Herrmann, A.; Rüttimann, M.; Crassous, J.; Cardullo, F.; Echegoyen, L.; Diederich, F. *J. Am. Chem. Soc.* **1998**, *120*, 7860−7868. (c) Kessinger, R.; Crassous, J.; Herrmann, A.; Rüttimann, M.; Echegoyen, L.; Diederich, F. *Angew. Chem. Int. Ed.* **1998**, *37*, 13−14. (d) Crassous, J.; Rivera, J.; Fender, N. S.; Shu, L.; Echegoyen, L.; Thilgen, C.; Herrmann, A.; Diederich, F. *Angew. Chem. Int. Ed.* **1999**, *38*, 1613−1671. (e) Kessinger, R.; Fender, N. S.; Echegoyen, L. E.; Thilgen, C.; Echegoyen, L.; Diederich, F. *Chem.*—*Eur. J.* **2000**, *6*, 2184−2192. (f) Lukoyanova, O.; Cardona, C. M.; Altable, M.; Filippone, S.; Domenech, Á. M.; Martín, N.; Echegoyen, L. *Angew. Chem. Int. Ed.* **2006**, *45*, 7430−7433.

(15) (a) Knight, B.; Martín, N.; Ohno, T.; Ortí, E.; Rovira, C.; Veciana, J.; Vidal-Gancedo, J.; Viruela, P.; Viruela, R.; Wudl, F. *J. Am. Chem. Soc.* **1997**, *119*, 9871−9882. (b) Beulen, M. W. J.; Rivera, J. A.; Herranz, M. Á.; Illescas, B.; Martín, N.; Echegoyen, L. *J. Org. Chem.* **2001**, *66*, 4393−4398.

C_{60}^{3-} is more reactive than C_{60}^{2-} under similar conditions.[11b,18] Recent reports on dinitrogen fixation[6a,c] and C=C, C=O, and $N-N^+$ bond reduction[6b] by an anionic γ-cyclodextrin-bicapped C_{60} complex under mild conditions have aroused interest to further study the reactivity of anionic C_{60} since it suggests that the chemistry of fullerenes is not completely understood as indicated by a recent review.[1f]

During our recent investigation into the reactivity of anionic C_{60}, an unexpected reaction involving trianionic C_{60}, water, and benzonitrile was discovered. Unlike previous studies, where the reducing potential was switched off when the number of coulombs reached the theoretical number required for a complete conversion of C_{60} to C_{60}^{2-},[8] in our case, the reducing potential was continuously applied to the anionic C_{60} benzonitrile solution after the theoretical number of coulombs had been reached. An unexpected *cis*-1 adduct of C_{60}, 1,4-dibenzyl-2,3-cyclic phenylimidate C_{60} (**1**), was regioselectively formed after the addition of benzyl bromide to the anionic C_{60} benzonitrile solution, while a related compound (**2**) bearing the same heterocycle as compound **1** was obtained from the anionic C_{60} benzonitrile solution when no benzyl bromide was added. A control experiment was performed where tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) was used instead of tetra-*n*-butylammonium perchlorate (TBAP) as the electrolyte, and the same product was obtained, indicating that the oxygen atom in compounds **1** and **2** is not from perchlorate ion but likely from traces of water present in solvent. In addition, reactivity of the neutral, monoanionic, dianionic, and trianionic C_{60} toward benzonitrile was examined. It showed that the real reactive species was the C_{60} trianion.

Herein, we report this unprecedented reaction which leads to the formation of C_{60} derivatives with cyclic phenylimidate. Although the detailed mechanism for the reaction remains to be elucidated by further work, we wish to report the structures of products and identify the reactive species for this novel reaction at the current stage.

Results and Discussion

Synthesis of 1,4-Dibenzyl-2,3-Cyclic Phenylimidate C_{60} (1). Fifty milligrams (69.4 μmol) of C_{60} was electroreduced at −1.10 V versus SCE in 50 mL of freshly distilled PhCN solution containing 0.1 M TBAP under either a nitrogen or an argon atmosphere. The procedures for the electrolysis are similar to previous work,[8g,i,j,n] except the reducing potential is continuously applied even after the theoretical number of coulombs required for a full conversion of C_{60} to C_{60}^{2-} has been reached. Notably, an extra irreversible anodic wave at −0.50 V versus SCE appears in addition to the redox waves of C_{60} (see Figure 1) as the reducing potential is continuously applied after the electrogeneration of C_{60}^{2-} is complete,[19] indicating a reaction involving anionic C_{60} has occurred. The extra irreversible anodic wave becomes stronger as the reducing potential is applied for a longer time. However, the cyclic voltammogram of the anionic C_{60} solution is completely distorted and featureless of the C_{60} moiety if the solution is kept under the external potential for too long, leading to the formation of more toluene or CS_2 insoluble product than when the anionic C_{60} solution is kept under the potential for less time. The potentiostat was switched off when the irreversible anodic wave at −0.50 V versus SCE became prominent, and at the same time, the features of C_{60} moiety were retained as shown in Figure 1, then 10 equiv of $PhCH_2Br$ was added to the solution all at once, and the reaction between the resulting anionic C_{60} benzonitrile solution and benzyl bromide was allowed to proceed for 40 min with stirring. The solvent was removed with a rotary evaporator under vacuum, and the residue was washed with methanol to remove TBAP before further purification.

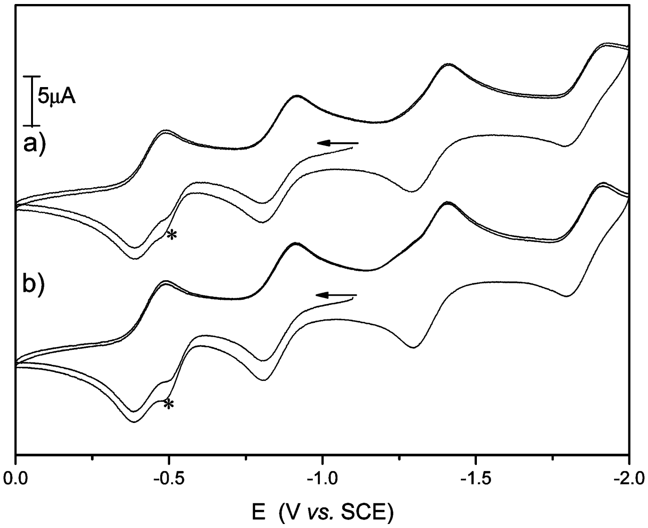


FIGURE 1. Cyclic voltammograms of the resulting anionic C_{60} with a coulometric value of slightly more than two electrons per molecule in benzonitrile solution containing 0.1 M TBAP under (a) Ar and (b) N_2.

Unlike previously reported results of reactions between C_{60}^{2-} and benzyl bromide,[8e,g,j,m,n] where the only major product is 1,4-$(PhCH_2)_2C_{60}$, a new major product, 1,4-dibenzyl-2,3-cyclic phenylimidate C_{60} (**1**), is found to be produced along with the formation of 1,4-$(PhCH_2)_2C_{60}$, trace amount of 1,2-$(PhCH_2)_2C_{60}$ (**3**), 1,2-$HPhCH_2C_{60}$ (**4**), [6,6]methanofullerene $C_{61}HPh$ (**5**), and unreacted C_{60} with retention times at 5.01, 5.60, 5.33, 6.58, 7.14, and 9.78 min, respectively, as shown in the HPLC trace of the reaction mixture (Figure 2). Notably, the HPLC trace over a Buckyprep column is nearly identical but reversed of that over a silica column reported previously, although it does not include compound **1**.[8n] The formation of 1,4-$(PhCH_2)_2C_{60}$, trace amount of 1,2-$(PhCH_2)_2C_{60}$ (**3**), 1,2-$HPhCH_2C_{60}$ (**4**), and [6,6]methanofullerene $C_{61}HPh$ (**5**) is typical for the reaction between the C_{60} dianion and benzyl bromide.[8n] However, the formation of compound **1** is unprecedented and suggests a novel reaction of anionic C_{60}. The results show that the real reactive species in this anionic C_{60} solution is C_{60}^{3-} as discussed below. Compound **1** was separated by gravity column chromatography over silica

---

(16) (a) Zhang, Y.; Liu, W.; Gao, X.; Zhao, Y.; Zheng, M.; Li, F.; Ye, D. *Tetrahedron Lett.* **2006**, *47*, 8571−8574. (b) Liu, W.; Zhang, Y.; Gao, X. *J. Am. Chem. Soc.* **2007**, *129*, 4973−4980.

(17) (a) Huang, Y.; Wayner, D. M. *J. Am. Chem. Soc.* **1993**, *115*, 367−368. (b) Niyazymbetov, M. E.; Evans, D. H. *J. Electrochem. Soc.* **1995**, *142*, 2655−2658. (c) Fuchigami, T.; Kasuga, M.; Konno, A. *J. Electroanal. Chem.* **1996**, *411*, 115−119. (d) D'Souza, F.; Choi, J.-P.; Hsieh, Y.-Y.; Shriver, K.; Kutner, W. *J. Phys. Chem. B* **1998**, *102*, 212−217. (e) Sherigara, B. S.; Kutner, W.; D'Souza, F. *Electroanal.* **2003**, *15*, 753−772.

(18) (a) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364−4366. (b) Beulen, M. W. J.; Echegoyen, L. *Chem. Commun.* **2000**, 1065−1066.

(19) It shows that the ambient conditions have a significant influence on the reaction. It requires the passing of much more excessive reducing charges in winter than in summer to have the irreversible anodic wave at −0.50 V versus SCE appear.

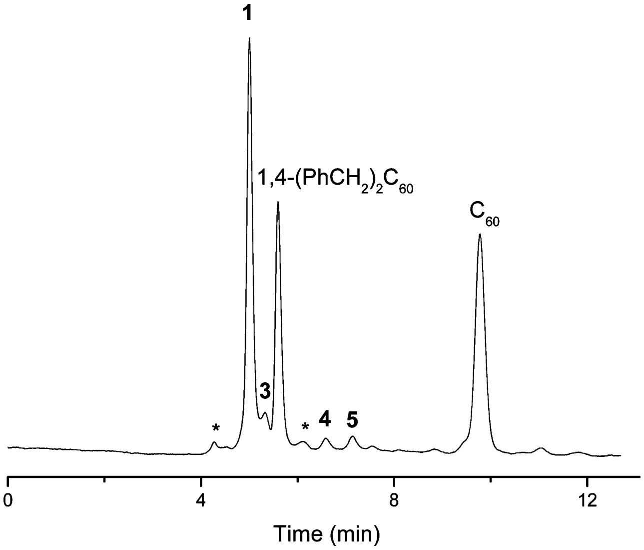


FIGURE 2. HPLC trace of the crude reaction mixture formed from the anionic C_{60} benzonitrile solution shown in Figure 1 and benzyl bromide. The mixture was eluted with toluene over a semipreparative Buckyprep column at a flow rate of 4.0 mL/min with the detector wavelength set at 380 nm. Peaks marked with 1, 3, 4, and 5 correspond to compounds of **1**, **3**, **4**, and **5**. Peaks marked with asterisks are not identified.

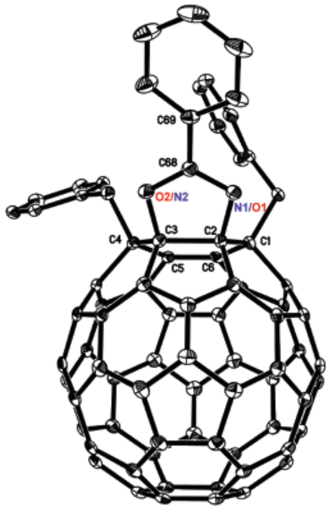


FIGURE 3. ORTEP diagram for one 1,4-dibenzyl-2,3-cyclic phenylimidate C_{60} molecule with 20% thermal ellipsoids. Hydrogen atoms and CS_2 molecule were omitted for clarity.

eluted by first using hexanes then a 1:3 v/v toluene/hexanes mixture. Under optimum conditions for producing compound **1**, the isolated yields for compound **1**, 1,4-$(PhCH_2)_2C_{60}$, and recovered C_{60} are ca. 35, 30, and 15%, respectively, while the total amount of 1,2-$(PhCH_2)_2C_{60}$ (**3**), 1,2-$HPhCH_2C_{60}$ (**4**), and [6,6]methanofullerene $C_{61}HPh$ (**5**) is less than 2%. The remainder of the reaction mixture is insoluble in toluene or CS_2 and remains to be identified.

X-ray Structure Characterization of Compound 1. Black needle-like crystals of compound **1** were obtained by slowly diffusing hexane into a CS_2 solution of compound **1** at room temperature. Figure 3 shows the X-ray single-crystal structure of compound **1**. It shows that two benzyl groups are bonded to C_{60} at C1 and C4, respectively, while a heterocycle is bonded to C_{60} via two heteroatoms at C2 and C3 positions. It is rational to designate one of the heteroatoms as a nitrogen atom since it actually consists of a benzonitrile molecule with the C$-C_6H_5$ group, indicating that the solvent, benzonitrile, takes part in the reaction. As for the second heteroatom, however, due to the similarity between nitrogen and oxygen atoms, its identity cannot be determined unambiguously from crystallography. It shows that it is reasonable to assign it as either a nitrogen (with a hydrogen atom on it) or an oxygen atom. Therefore, it has to rely on further characterizations to determine the identity of this heteroatom. As discussed below, it shows that the second heteroatom is an oxygen atom, and the heterocycle is therefore an oxazoline.

The bond lengths for C1$-$C2 and C3$-$C4 are 1.581(5) and 1.583(5) Å, which are within the range for a C$-$C single bond length. For C2$-$C3, it is 1.624(5) Å, which is remarkably elongated with respect to a C$-$C single bond. A similar bond length elongation for this bond has also been observed in compounds with a *cis*-1 pattern.[20] The bond lengths for C4$-$C5 and C1$-$C6 are 1.526(5) and 1.524(5) Å, respectively, whereas it is 1.363(5) Å for C5$-$C6, and they are all within the bond length range for C_{60}. The C1$-$C2$-$C3$-$C4$-$C5$-$C6 ring is distorted, with C1 and C4 being uplifted by 0.128 and 0.121 Å from the mean plane, respectively. The bond angles of C69$-$C68$-$N1/O1 and C69$-$C68$-$O2/N2 are 120.3(4) and 121.7(4)°, respectively, and the sum of bond angles of C69$-$C68$-$N1/O1, C69$-$C68$-$O2/N2, and N1/O1$-$C68$-$O2/N2 is 360°, indicating that C68 is an sp^2 carbon atom. The measured bond lengths for N1/O1$-$C68 and O2/N2$-$C68 (C$=$N and C$-$O) are almost identical with the values of 1.328(5) and 1.319(5) Å, respectively, which is in agreement with the reported values for crystal structures of oxazolines[21] and is probably due to the delocalization of π-electrons among N$=$C$-$O bonds.[21b] The bond lengths for N1/O1$-$C2 and O2/N2$-$C3 (C$-$N and C$-$O) are also almost identical with the values of 1.469(4) and 1.478(4) Å, which are consistent with the corresponding bond length for typical oxazolines.[21] It is noteworthy that, since the oxazoline is located at the [5,6] bond of C_{60} and there is no symmetry plane cutting either through or perpendicular to the plane of the imidate, compound **1** should thus have a C_1 symmetry and be a racemic mixture.

UV$-$Visible Spectrum of Compound 1. Figure 4 shows the UV$-$visible spectrum of compound **1** in hexane. It has absorption bands at 206 and 256 nm, which are also observed in the spectrum of C_{60}.[22] A weak broad absorption band at around 336 nm is observed, which is very different from the sharp and strong absorption band for C_{60} appearing in the same region.[22] The compound also exhibits a spike at 429 nm, which is characteristic for C_{60} derivatives with 1,2-addition pattern including 1,2-[8j,23] and *cis*-1 adducts,[20b,24] and it is therefore consistent with the *cis*-1 structural assignment for the compound.

NMR of Compound 1. Figure 5 shows the ^1H NMR of compound **1** from 4.0 to 9.0 ppm recorded in CS_2 with C_6D_6 as the external lock, a full spectrum is shown in the Supporting Information. Two AB quartets I (aa) and II (bb) centered at 4.76 and 4.72 ppm are observed, which are due to the methylene protons of benzyls,[8j] indicating the molecule has a C_1 symmetry

---

[20] (a) Miller, G. P.; Tetreau, M. C.; Olmstead, M. M.; Lord, P. A.; Balch, A. L. *Chem. Commun.* **2001**, 1758−1759. (b) Murata, Y.; Suzuki, M.; Rubin, Y.; Komatsu, K. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1669−1672.

[21] (a) Braunstein, P.; Graiff, C.; Naud, F.; Pfaltz, A.; Tiripicchio, A. *Inorg. Chem.* **2000**, *39*, 4468−4475. (b) McPherson, L. D.; Drees, M.; Khan, S. I.; Strassner, T.; Abu-Omar, M. M. *Inorg. Chem.* **2004**, *43*, 4036−4050.

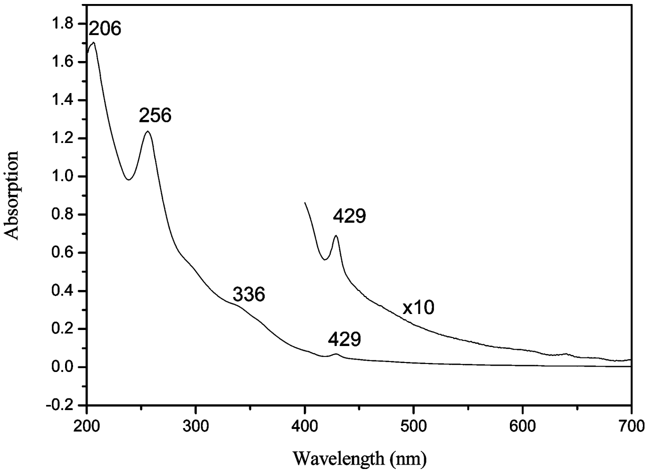


FIGURE 4. UV−visible spectrum of compound **1** in hexane.

and is consistent with the X-ray single-crystal diffraction results. Resonances arising from the aromatic protons are also present in the spectrum. Peaks at 8.79 (d, 2H), 8.06 (t, 1H), and 8.02 (t, 2H) ppm are assigned to the phenyl protons of the heterocycle, while resonances at 7.75 (d, 4H) and from 7.62 to 7.51 (m, 6H) ppm are due to the phenyl protons of benzyl groups[8j] and partly overlap with those from the toluene residue used for purification of the compound. Notably, no resonance corresponding to the amine proton is observed for the compound in the solvent system where the possibility of H−D exchange is avoided, indicating that no amine group is present in the molecule, which is in agreement with the assignment of the heteroatom as an oxygen atom.

Figure 6 shows the ^{13}C NMR of **1** recorded in a mixture of CS_2 and $CDCl_3$. Two resonances corresponding to the methylene carbons of the benzyl groups are shown at 46.6 and 45.9 ppm, while resonances corresponding to the two sp^3 C_{60} carbons bonded to benzyls are shown at 62.9 and 61.9 ppm. These values are in agreement with a previous report on 1,4-dibenzyl C_{60}.[8j] The resonances at 91.5 and 98.0 ppm are assigned to the two sp^3 C_{60} carbons bonded to the nitrogen and oxygen atoms, consistent with literature values.[24,25] A total of 62 resonances are shown in the sp^2 region, while 49 of them are assigned to the sp^2 carbons of C_{60} from 153.4 to 135.3 ppm. The resonance at 162.9 ppm is due to the imine carbon of the cyclic phenylimidate, and the remaining 12 resonances from 134.9 to 126.9 ppm are from the phenyl carbons of the heterocycle and benzyl groups. The results are in agreement with the structural assignment of compound **1**, as displayed by the X-ray single-crystal diffraction.

MALDI TOF Mass Spectrum of Compound 1. Compound **1** was subject to MALDI TOF MS measurement using 2,5-dihydroxybenzoic acid (DHB) as the matrix. However, efforts to obtain accurate molecular weight by FT-ICR MS were not successful. Figure 7 shows the positive MALDI TOF mass spectrum of **1**. It shows the protonated molecular ion $[M + H]^+$ at $m/z = 1022$, consistent with the structural assignment for the compound. Ions at 930, 839, 810, 797, and 720 correspond to the fragment ions. The oxygen adduct is shown at 736, which is likely from a fragmentation process of the compound or a possible gas-phase reaction with the matrix as observed in previous studies.[8i]

Synthesis of [6,6] Cyclic Phenylimidate C_{60} (2). In order to have a better understanding of the reaction, experiments were performed where the procedures were exactly the same as those for the generation of compound **1**, except no benzyl bromide was added to the anionic C_{60} benzonitrile solution shown in Figure 1. The solution was then oxidized back to neutral electrochemically. The procedures for purification of the compound are similar to that for compound **1**. Figure 8 shows the HPLC trace of the crude reaction mixture. A new compound characterized as [6,6] cyclic phenylimidate C_{60} (**2**) (Chart 1) appeared in the HPLC at 7.51 min along with the fraction peak of unreacted C_{60} at 9.74 min. Under optimum conditions, the isolated yields are ca. 10 and 70% for **2** and recovered C_{60}, respectively, while the remaining product is insoluble in either toluene or CS_2 and remains to be identified.

NMR of Compound 2. Figure 9 shows the ^1H NMR of compound **2** from 4.0 to 9.0 ppm, while a full spectrum is shown in the Supporting Information. Similar to the spectrum of compound **1**, resonances are shown at 8.82 (d, 2H), 8.08 (t, 1H), and 8.02 (t, 2H) ppm, which correspond to the protons of the phenyl ring of phenylimidate group, indicating the existence of phenylimidate in the molecule. The results are further confirmed by the observation that no resonance from the amine proton is shown in the spectrum, consistent with the assignment of the second heteroatom as an oxygen atom. As expected, no resonances from methylene protons of benzyls are observed, suggesting no benzyls are present in compound **2**. Notably, a

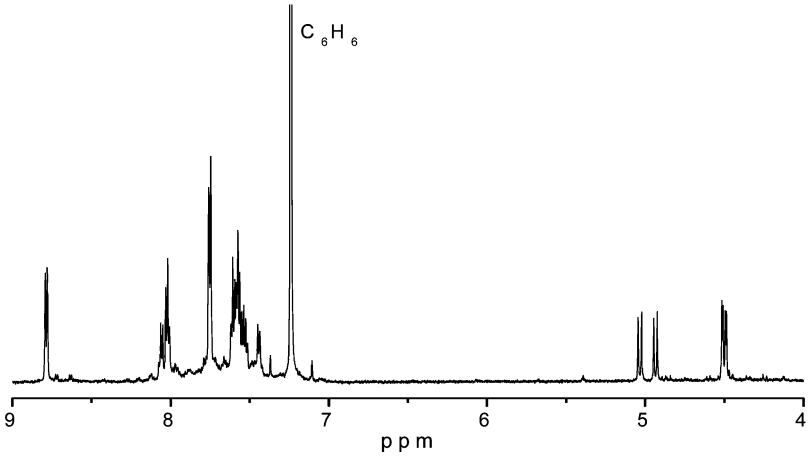


FIGURE 5. ^1H NMR spectrum of compound **1** in CS_2 recorded on a 600 MHz instrument. C_6D_6 was used as the external lock solvent.

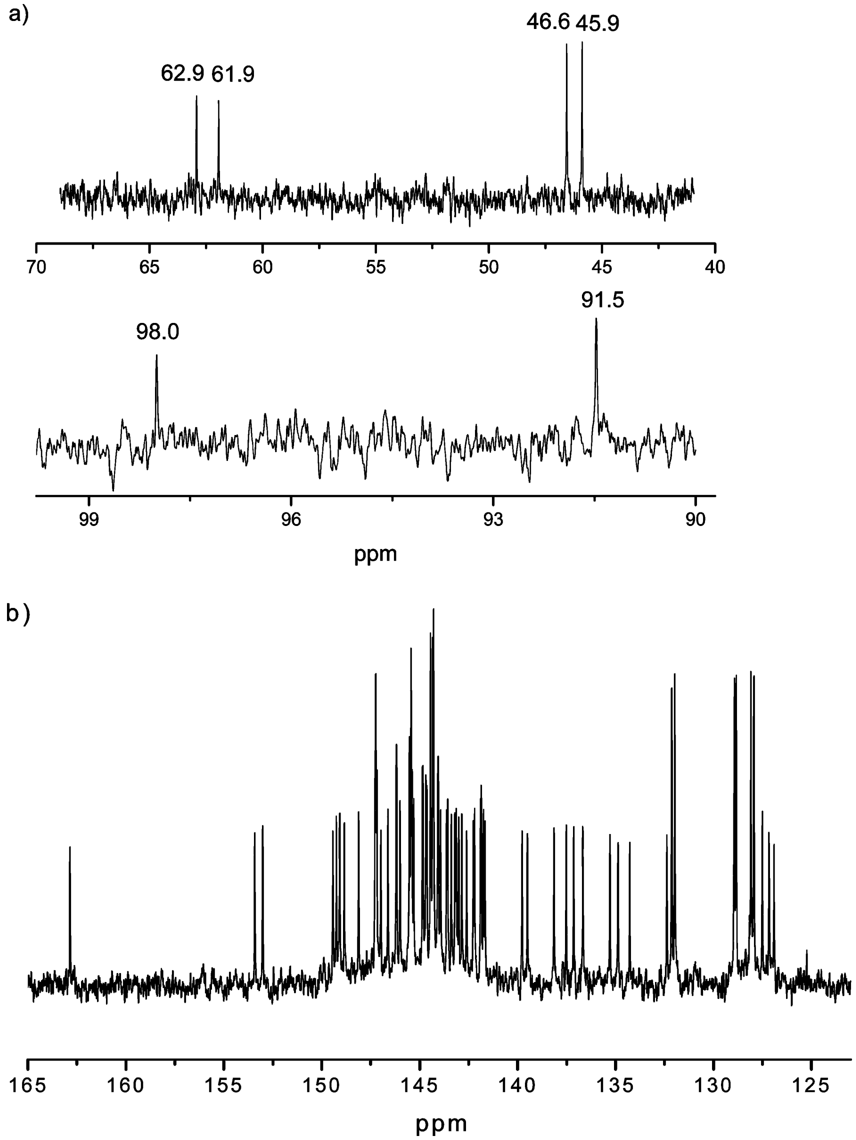


FIGURE 6. ^{13}C NMR spectrum of **1** in $CS_2/CDCl_3$ for (a) sp^3 carbons and (b) sp^2 carbons recorded on a 150 MHz instrument.

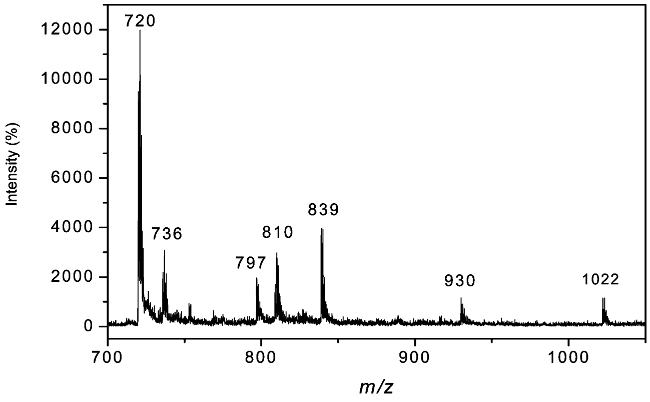


FIGURE 7. Positive MALDI TOF MS of compound **1**.

small amount of toluene is always shown in the spectrum even though the compound was put under vacuum for several days, indicating that there might be some interactions between compound **2** and toluene.

Figure 10 shows the ^{13}C NMR of compound **2**. Two weak sp^3 carbons of C_{60}, probably due to longer relaxation time of the carbons, are observed at 91.6 and 96.6 ppm, which are attributed to the two sp^3 carbons connected to the nitrogen and oxygen atoms,[24,25] indicating the presence of a cyclic phenylimidate group as in compound **1**. A total of 31 resonances for the sp^2 carbon atoms of the compound appear in the spectrum, while 26 of them are assigned to C_{60} carbons from 147.5 to 135.4 ppm, and four resonances are assigned to the phenyl carbons at 131.7 (1 C, Ph), 128.7 (2C, Ph), 128.1 (2C, Ph), and 126.5 (1C, Ph) ppm, and the remaining one at 164.3 ppm is from the imine

---

(22) Hare, J. P.; Kroto, H. W.; Taylor, R. *Chem. Phys. Lett.* **1991**, *177*, 394−398.

(23) (a) Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231−1250. (b) Linssen, T. G.; Dürr, K.; Hanack, M.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 103−104.

(24) (a) Ulmer, L.; Siedschlag, C.; Mattay, J. *Eur. J. Org. Chem.* **2003**, 3811−3817. (b) Schick, G.; Hirsch, A.; Mauser, H.; Clark, T. *Chem.− Eur. J.* **1996**, *2*, 935−943.

(25) Wang, G.-W.; Li, F.-B.; Xu, Y. *J. Org. Chem.* **2007**, *72*, 4774−4778.

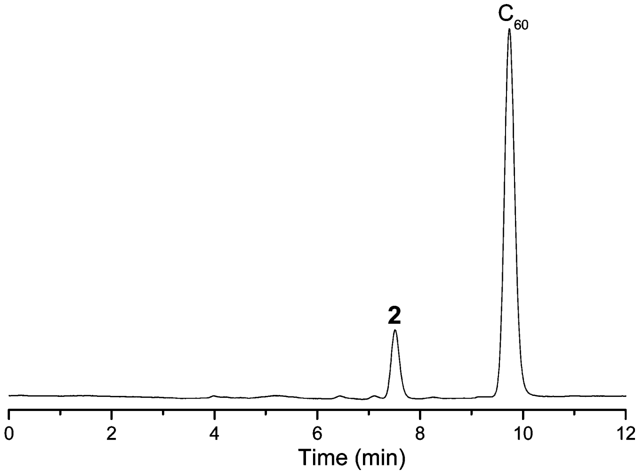


FIGURE 8. HPLC trace of the crude reaction mixture formed from the anionic C_{60} benzonitrile solution shown in Figure 1. The mixture was eluted by toluene over a semipreparative Buckyprep column at a flow rate of 4.0 mL/min with the detector wavelength set at 380 nm.

carbon of the phenylimidate group. Resonances at 136.6, 128.3, 127.6, and 124.8 ppm are due to the toluene residue used for purification of the compound. The appearance of only 26 C_{60} carbons indicates that the compound possesses a C_s symmetry, and it indicates that, unlike the compound **1**, the cyclic phenylimidate group in compound **2** has to be on a [6,6] bond of C_{60} rather than a [5,6] bond; otherwise, compound **2** would have a C_1 symmetry because there is no symmetry plane cutting either through or perpendicular to the plane of the oxazoline. Since compound **2** was obtained from the same anionic C_{60} benzonitrile solution as compound **1**, except no benzyl bromide was added, it is reasonable that the two compounds are related by bearing the same adduct due to a similar reaction. However, it is noteworthy that the two structures have different addition positions for phenylimidate, which is probably due to the further addition of 1,4-dibenzyls in compound **1**.

MALDI FT-ICR Mass Spectrum of Compound 2. The identity of the heterocycle was determined to be a cyclic phenylimidate unambiguously by the MALDI FT-ICR mass spectrum of compound **2** using 2,5-dihydroxybenzoic acid (DHB) as the matrix. Figure 11 shows the positive MALDI FT-ICR mass spectrum of **2**, and Table 1 lists the calculated and experimental m/z values for the observed peaks. The protonated monoisotopic molecular ion is shown at $m/z = 840.04214$ as the base peak, while ions appearing at 841.04535, 842.04878, and 843.05378 are due to the isotopic peaks since the mass difference between them is around 1.003. A relatively small peak is observed at 839.03437, which has a 1.008 mass difference with the base peak at 840.04214, indicating that the difference is caused by a proton; it is therefore reasonable to assign the peak at 839.03437 as the molecular ion. Fragment ions are also observed in the spectrum, and their identities are listed in Table 1. The observed m/z values all have an excellent agreement with the theoretical values, confirming that the heterocycle is a cyclic phenylimidate ring. Considering that compounds **1** and **2** should have the same heterocycle according to NMR results and similar synthetic methods, it is reasonable to assign the unresolved heteroatom in the crystal structure of compound **1** as an oxygen atom.

UV−Visible Spectrum of Compound 2. Figure 12 shows the UV−visible spectrum of compound **2** in hexane. It has three major absorption bands at 207, 255, and 314 nm along with a weak shoulder absorption band at 415 nm. The bands at 207 and 255 nm are also observed in the spectrum of C_{60}[22] and are probably due to the electronic transitions of C_{60}. The absorption at 314 nm is blue-shifted with respect to the 330 nm absorption band of C_{60};[22] however, it is not usually shown in the spectra for C_{60} derivatives where the adducts are bonded to C_{60} via carbon atoms but observed in the spectrum of C_{60} derivatives with at least one heteroatom connected directly to C_{60}.[25,26] The absorption band is therefore probably related to the type of atoms bonded to C_{60}. Notably, no absorption around 428 nm, which is characteristic feature for C_{60} derivatives with 1,2-pattern,[7e] is shown in the spectrum, although the compound is a [6,6] derivative. The absence of this absorption peak has been previously reported for [6,6] C_{60} derivatives with a cyclic imidate group,[26a] indicating the origin of the absorption at 428 nm might also be associated with the type of atoms bonded to C_{60} in addition to the addition pattern.

Reactive Species: C_{60}^{2-} or C_{60}^{3-}? The reactivity of the C_{60} dianion has been studied in benzonitrile, and no such reaction has been reported.[8a,d−g,i,j,m,n,11a,c] Notably, it requires more reducing charges than the theoretical number for the conversion of C_{60} to C_{60}^{2-} to have the reaction. It is therefore possible that the real reactive species for the reaction is not the C_{60} dianion, but the trianion instead.

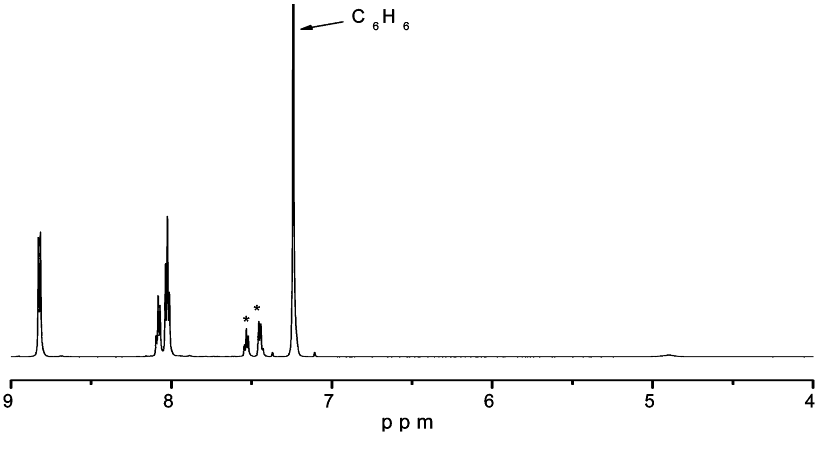


FIGURE 9. ^1H NMR spectrum of compound **2** in CS_2 recorded on a 600 MHz instrument. C_6D_6 was used as the external lock solvent. Peaks marked with asterisks are from toluene residue used for purifying **2**.

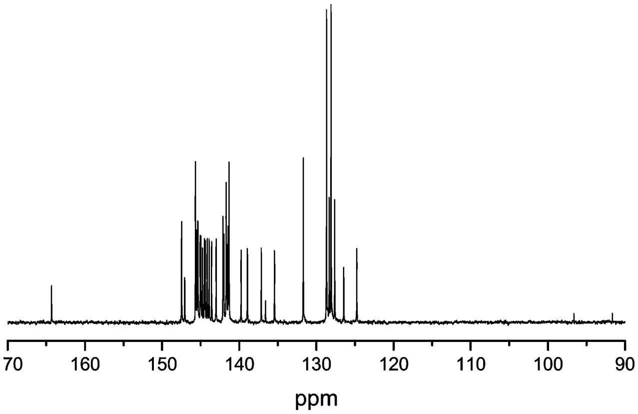


FIGURE 10. ^{13}C NMR spectrum of compound **2** in CS_2 recorded on a 150 MHz instrument. DMSO-d_6 was used as the external lock solvent.

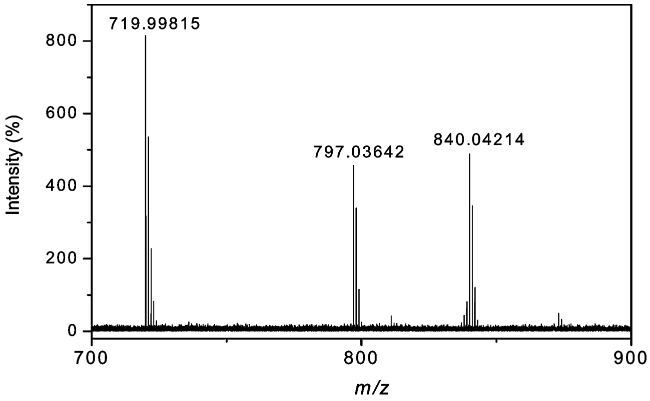
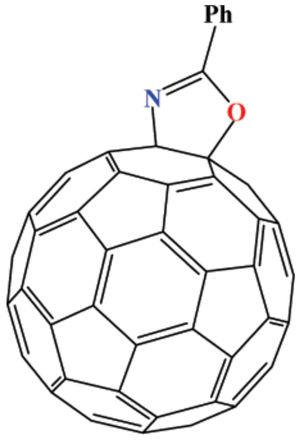


FIGURE 11. Positive MALDI FT-ICR HRMS of compound **2**.

CHART 1. Compound 2



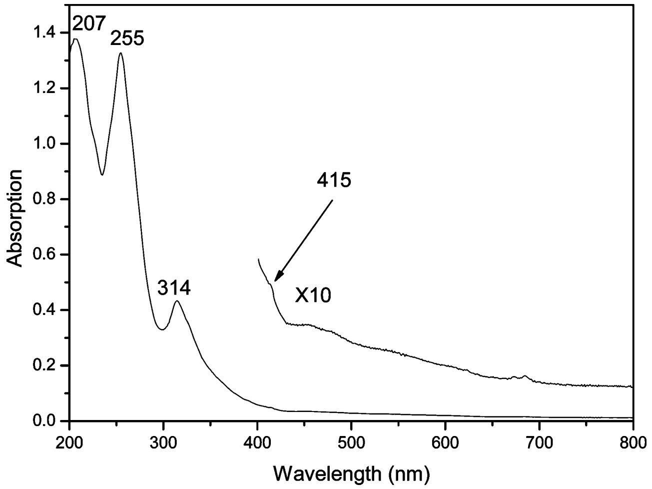


FIGURE 12. UV−vis spectrum of compound **2** in hexane.

TABLE 1. Calculated and Observed *m/z* Values for Molecular and Fragment Ions of Compound 2

species	calculated *m/z*	observed *m/z*	deviation (ppm)
$[C_{67}H_5NO + H]^+$	840.04494	840.04214	−3.3
$C_{67}H_5NO^+$	839.03711	839.03437	−3.3
$C_{66}H_5^+$	797.03913	797.03642	−3.4
C_{60}	720.00000	719.99815	−0.3

To probe further into the reaction, control experiments were carried out where the reactivity of neutral, monoanionic, dianionic, and trianionic C_{60} was examined toward benzonitrile. For neutral C_{60}, the total reaction time (since C_{60} was put into benzonitrile) was about 3 h, which is the typical total reaction time for the generation of compound **2** from the anionic C_{60} solution. As for the reaction of monoanionic C_{60}, it was generated with a reducing potential of −0.70 V versus SCE, and the reducing potential was continuously applied after C_{60}^- was fully generated, and the total reaction time was also 3 h. For the reaction of the dianionic C_{60}, the reduction was stopped once the number of electrons reached 90% of the theoretical number required for the conversion to C_{60}^{2-}. As for trianionic C_{60}, it was generated electrochemically with a reducing potential of −1.60 V versus SCE in benzonitrile, and the electrolysis was terminated once the theoretical number of coulombs required for the conversion of C_{60} to C_{60}^{3-} was reached. Notably, the cyclic voltammogram of the resulting C_{60}^{3-} is very similar to that of the anionic C_{60} benzonitrile solution shown in Figure 1, with the appearance of the irreversible anodic peak at around −0.50 V versus SCE. For the anionic C_{60} solutions, the anions were oxidized back to neutral electrochemically by applying 0 V versus SCE at the end of the experiment. The workup for the purification of the reaction products from the control experiments is the same as those for the isolation of compound **2**. Figure 13 shows the HPLC traces of the crude products obtained from neutral and different anionic species of C_{60}.

As shown in the figure, there is no reaction product for the neutral, monoanionic, and dianionic C_{60} benzonitrile solution. While a significant amount of compound **2** (retention time = 7.50 min, and confirmed by UV−vis measurement) was obtained from the C_{60}^{3-} benzonitrile solution with an isolation yield of ca. 50%, which is much higher than that obtained from the anionic C_{60} solution shown in Figure 1, indicating that C_{60}^{3-} is the real reactive species for the observed reaction in the anionic C_{60} benzonitrile solution.

In fact, it is not straightforward to perceive that the C_{60} trianion can be generated in significant amount in a solution where the reducing potential (−1.10 V vs SCE) is about 220 mV less negative than the half-wave potential of $C_{60}^{2-/3-}$ (−1.32 V vs SCE)[27] since, according to Nernst law, the amount of C_{60}^{3-} is only about 0.02% at equilibrium. However, the fact that the reaction requires the passing of excessive reducing charges to

---

(26) (a) Banks, M. R.; Cadogan, J. I. G.; Gosney, I.; Hodgson, P. K. G.; Langridge-Smith, P. R. R.; Rankin, D. W. H. *J. Chem. Soc., Chem. Commun.* **1994**, 1365−1366. (b) Grösser, T.; Parto, M.; Lucchini, V.; Hirsh, A.; Wudl, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1343−1345.

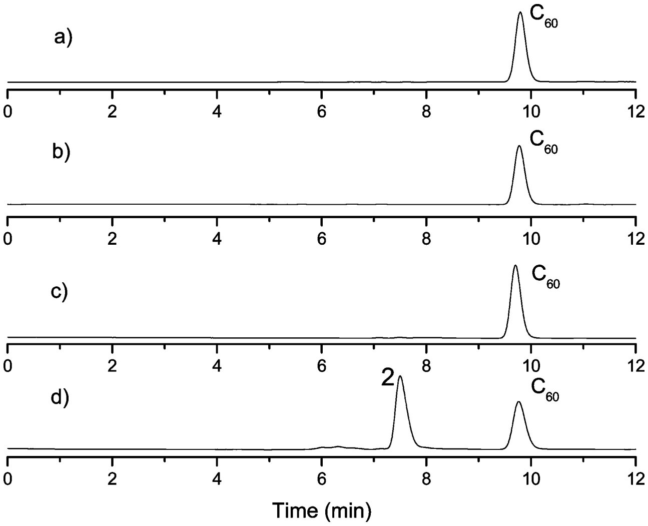


FIGURE 13. HPLC traces of crude mixture from benzonitrile solution of (a) neutral C_{60}, (b) monoanionic C_{60}, (c) 90% electrolyzed dianionic, and (d) trianionic C_{60}. The mixture was eluted by toluene over a semipreparative Buckyprep column at a flow rate of 4.0 mL/min with the detector wavelength set at 380 nm.

proceed suggests that C_{60}^{2-} is unlikely the real reactive species for the reaction. Previous studies on the electrogenerated C_{60} dianion have shown that it is inert toward solvent containing a nitrile functional group such as benzonitrile and acetonitrile,[8,11a−c] and no formation of compounds **2** or **1** has been reported from electrogenerated dianionic C_{60} benzonitrile solution or reaction of the C_{60} dianion with benzyl bromide, confirming that the C_{60} dianion is unlikely the real reactive species for the reaction. Notably, previous work on the ESR studies of the C_{60} monoanion suggests the possibility that a significant amount of higher C_{60} anions can be generated at a less negative reducing potential. It has been shown that there is often a narrow spike in addition to the broad line width signal present in the ESR spectrum of the C_{60} monoanion.[9c,11b−f] Recent studies have shown that the spike is due to a trace amount of C_{60} derivatives formed by the reaction of higher C_{60} anions present in the C_{60} monoanion solution,[11e,f] indicating that higher C_{60} anions can be generated at a much less negative potential. Although the intensity of the spike is not related directly to the amount of C_{60} dianion present in the solution since C_{60} dianion is ESR silent,[9c] the amount of C_{60} dianion does have a significant effect on the intensity of the spike since it affects the amount of C_{60} derivatives formed in the solution. Theoretically, only a very small amount of C_{60}^{2-} can be generated at a reducing potential set for the electrogeneration of the C_{60} monoanion;[11d] however, it has been observed that the intensity of the spike in the ESR spectrum for the C_{60} monoanion increases significantly as the electrolysis is carried out with a coulometric value of more than one electron per C_{60} molecule,[11c,e,f] indicating that the amount of higher C_{60} anion can be much higher than theoretical prediction under more reducing conditions. It is therefore possible that a significant amount of C_{60}^{3-} can be generated when more than a theoretical number of reducing charges is transferred, even though the reducing potential is less negative than the half-wave potential of C_{60}^{2-}/C_{60}^{3-}.

Origin of Oxygen Atom in the Cyclic Phenylimidate. Since TBAP could be a possible oxygen source for the reaction, a control experiment was performed where tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) was used as the electrolyte instead of TBAP. The same product was obtained as shown by HPLC, UV−vis, and ^1H NMR characterizations, indicating that it is unlikely that the oxygen atom is from the perchlorate ions used in the experiment. Due to the high sensitivity of C_{60} anions toward oxygen, the reaction was carried out under inert atmosphere with ultrahigh purity, and it is unlikely that C_{60}^{3-} could be generated if there were traces of oxygen in the system. Therefore, under the experimental conditions, the most likely source for the oxygen atom is traces of water, which may exist in the solvent and glassware used for experiment. Benzonitrile is known to have some common impurities such as water, benzoic acid, isonitriles, and different amines.[28] It has been shown that benzonitrile suitable for electrochemical study can be obtained by distillation over phosphorus pentoxide at reduced pressure.[28] An irreversible wave corresponding to water reduction is shown at around −1.90 V versus SCE in undistilled benzonitrile, which interferes severely with the fourth redox process of C_{60}, and it is not suitable for electrochemical generation of C_{60} anions. In contrast, when distilled benzonitrile is used, no irreversible wave corresponding to water reduction at around −1.90 V versus SCE is observed, and the fourth redox process of C_{60} is nicely displayed in the cyclic voltammogram along with the first three redox processes. However, traces of water might still exist in the distilled benzonitrile even if it is suitable for electrochemical study and generation of C_{60} anions. Eaton et al. have reported that even under a much more strict drying condition, where the solvent was kept over 4 Å molecular sieves for 24 h at 400 °C, 10^{-6} Torr, trace water was still considered to be the major impurity in the solvent.[11b]

Conclusion

This report demonstrates a novel type of reaction of C_{60}^{3-} with benzonitrile and water. Several C_{60} derivatives with cyclic phenylimidate have been obtained and characterized by ^1H NMR, ^{13}C NMR, MALDI MS, UV−vis, and X-ray single-crystal diffractions. Control experiments of neutral, monoanionic, dianionic, and trianionic C_{60} have shown that the C_{60} trianion is the real reactive species for the reaction. The origin of the oxygen atom is attributed to traces of water present in the system. The reported reaction provides a promising method for preparation of heterocyclic C_{60} derivatives and opens up new perspectives on fullerene chemistry. Further studies on the reaction mechanism are currently under investigation in the laboratory.

Experimental Section

Spectral Characterization of 1,4-Dibenzyl-2,3-Cyclic Phenylimidate C_{60} (1): Positive MALDI TOF MS *m/z* 1022(MH^+); UV−vis (hexane) $\lambda_{max} = 206, 256, 336, 429$ nm; ^1H NMR (600 MHz, in CS_2, C_6D_6 was used as the external lock solvent) δ 8.79 (d, 2H), 8.06 (t, 1H), 8.02 (t, 2H), 7.75 (d, 4H) and from 7.62 to 7.51 (m, 6H), 5.03 (d, 1H), 4.94 (d, 1H), 4.51 (d, 1H), 4.49 (d, 1H); ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) δ 162.9 (1C, C=N), 153.4 (1C), 153.0 (1C), 149.4 (1C), 149.3 (1C), 149.1 (1C), 148.9 (1C), 148.1 (1C), 147.3 (1C), 147.2 (2C), 147.2 (1C), 147.0 (1C), 146.6

---

[27] Dubois, D.; Moninot, G.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* **1992**, *96*, 7137−7145.

[28] Kadish, K. M.; Anderson, J. E. *Pure Appl. Chem.* **1987**, *59*, 703−714.

(1C), 146.2 (1C), 146.0 (1C), 145.5 (2C), 145.4 (2C), 145.4 (1C), 145.3 (1C), 144.9 (1C), 144.7 (1C), 144.6 (1C), 144.5 (2C), 144.3 (2C), 144.3 (2C), 144.1 (2C), 144.1 (1C), 144.0 (1C), 143.9 (1C), 143.6 (1C), 143.6 (1C), 143.4 (1C), 143.2 (1C), 143.1 (1C), 143.0 (1C), 142.9 (1C), 142.6 (1C), 142.3 (1C), 142.2 (1C), 141.9 (1C), 141.9 (1C), 141.7 (1C), 141.7 (1C), 139.8 (1C), 139.5 (1C), 138.1 (1C), 137.5 (1C), 137.1 (1C), 136.7 (1C), 135.3 (1C), 134.9 (1C, Ph), 134.3 (1C, Ph), 132.4 (1C, Ph), 132.1 (2C, Ph), 132.0 (2C, Ph), 128.9 (2C, Ph), 128.8 (2C, Ph), 128.1 (2C, Ph), 127.9 (2C, Ph), 127.5 (1C, Ph), 127.2 (1C, Ph), 126.9 (1C, Ph), 98.0 (1C, sp^3, C−O), 91.5 (1C, sp^3, C−N), 62.9 (1C, sp^3, C−CH_2Ph), 61.9 (1C, sp^3, C−CH_2Ph), 46.6 (1C, CH_2), 45.9 (1C, CH_2).

X-ray Single-Crystal Diffraction of 1,4-Dibenzyl-2,3-Cyclic Phenylimidate C_{60} (1). Black needle-like crystals of **1** were obtained by slowly diffusing hexane into a CS_2 solution of **1** at room temperature. Single-crystal X-ray diffraction data were collected on a Bruker SMART Apex equipped with a CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) in the scan range 1.65° < θ < 25.03°. The structure was solved with the direct method of SHELXS-97 and refined with full-matrix least-squares techniques using the SHELXL-97 program within WINGX. Crystal data of **1**·0.5 CS_2: $C_{81.50}H_{19}NOS$, M_w = 1060.04, triclinic, space group $P\bar{1}$, a = 9.9186(8) Å, b = 12.4763(10) Å, c = 18.4869(14) Å, α = 93.812(2)°, β = 104.287(2)°, γ = 95.025(2)°, V = 2199.2(3) Å^3, z = 2, D_{calcd} = 1.601 Mg m^{-3}, μ = 0.139 mm^{-1}, T = 187(2) K, crystal size 0.23 × 0.16 × 0.10 mm; reflections collected 11 403, independent reflections 7612; 4493 with $I > 2\sigma(I)$; $R_1 = 0.0698$ [$I > 2\sigma(I)$], w$R_2 = 0.1431$ [$I > 2\sigma(I)$]; $R_1 = 0.1258$ (all data), w$R_2 = 0.1713$ (all data), GOF (on F^2) = 1.026.

Spectral Characterization of [6,6] Cyclic Phenylimidate C_{60} (2): MALDI FT-ICR MS m/z calcd for $C_{67}H_5NO$ $[M + H]^+$ 840.04494, found 840.04214; UV−vis (n-hexane) for **2** $\lambda_{\max}$ = 207, 255, 314, and 415 nm; ^{1}H NMR (600 MHz, in CS_2, C_6D_6 was used as the external lock solvent) δ 8.82 (d, 2H), 8.08 (t, 1H) and 8.02 (t, 2H); ^{13}C NMR (150 MHz, CS_2, DMSO-d_6 was used as external lock solvent) δ 164.3 (1C, C═N), 147.5 (2C), 147.1 (1C), 145.7 (4C), 145.5 (2C), 145.4 (2C), 145.3 (2C), 145.1 (2C), 145.0 (2C), 145.0 (2C), 144.8 (2C), 144.5 (2C), 144.4 (2C), 143.9 (2C), 143.6 (2C), 143.0 (2C), 142.1 (3C), 142.1 (2C), 142.0 (2C), 141.7 (4C), 141.6 (2C), 141.4 (2C), 141.3 (4C), 139.8 (2C), 138.9 (2C), 137.1 (2C), 135.4 (2C), 96.6 (1C, sp^3, C−O), 91.6 (1C, sp^3, C−N), 131.7 (1 C, Ph), 128.7 (2C, Ph), 128.3 (2C, Ph), 126.5 (1C, Ph).

Acknowledgment. We thank the reviewers of the manuscript for their deep insights and constructive remarks. We thank Professors Luis Echegoyen, Karl Kadish, and Shuichi Fukuzumi for inspiring discussions. The work was partly supported by Hundred Talents Program of the Chinese Academy of Sciences, NSFC International Collaboration Grants 00550110367 and 00650110171.

Supporting Information Available: General experimental methods, the CIF file for 1,4-dibenzyl-2,3-cyclic phenylimidate C_{60}, ^{1}H NMR spectra of **1**, **2**, and the product isolated from the reaction mixture of C_{60}^{3-} benzonitrile solution where 0.1 M tetra-n-butylammonium hexafluorophosphate ($TBAPF_6$) was used as electrolyte, and ^{13}C NMR spectra of compound **1**, **2**, and the expanded region from 148 to 124 ppm for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO702678C