Synthesis and Properties of the First Acetylene Derivatives of C_{60}

Koichi Komatsu,[*,†] Yasujiro Murata,[†]
Naohiko Takimoto,[†] Sadayuki Mori,[†]
Nobuyuki Sugita,[†] and Terence S. M. Wan[‡]

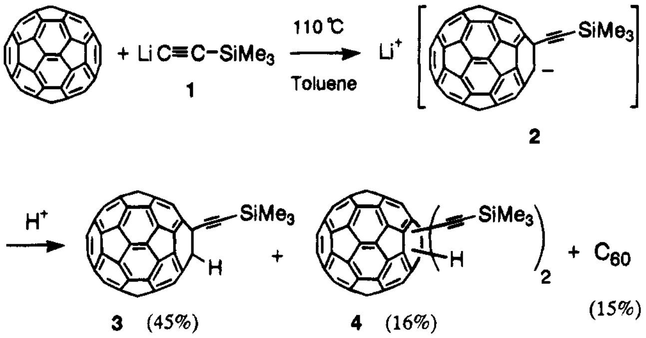
*Institute for Chemical Research, Kyoto University,
Uji, Kyoto-fu 611, Japan, and Department of Chemistry,
The Hong Kong University of Science and Technology,
Clear Water Bay, Kowloon, Hong Kong*

Received June 1, 1994

Study of the chemical transformation of fullerene C_{60} is a widely expanding field of organic chemistry and has led to formation of various C_{60} derivatives.[1] However there has been no report on the acetylene derivative of C_{60}, although such a compound could be a versatile precursor to a variety of new molecules. It should also be of interest to examine the electronic effects of the triple bond upon the redox behavior of the C_{60} core.[2] We now report the preparation and properties of (trimethylsilyl)ethynyl- and phenylethynylfullerenes, the first alkyne C_{60} derivatives.

It has been shown by Hirsch,[3a,b] Fagan,[3c] and coworkers that the reaction of C_{60} with various organolithium and Grignard reagents gives well-characterized monoadducts of C_{60} having various alkyl or phenyl groups.[4] Compared with these reagents, metal acetylides were anticipated to be much less reactive toward C_{60} due to their stability and low nucleophilicity. In fact, no reaction was observed when excess [(trimethylsilyl)ethynyl]lithium (**1**) was added to a solution of C_{60} in toluene at room temperature. However, the desired addition of **1** did occur in refluxing toluene. Thus, to a refluxing solution of C_{60} in toluene there was slowly added dropwise over 2 min 4 equiv of a THF solution of **1** with vigorous stirring. The resulting black suspension, which contains the lithium salt **2** of ethynylated C_{60}, was quenched with excess trifluoroacetic acid to give a dark brown solution. Chromatographic separation of the crude product afforded monoadduct **3** and bis-adduct **4**, both as dark brown powders in 45 and 16% yield, respectively, while unchanged C_{60} was recovered in 15% yield (Scheme 1). The product yields were highly dependent on reaction conditions, particularly on exclusion of oxygen and moisture and the efficiency of stirring during the addition.

Scheme 1



Monoadduct **3** exhibited a ^1H NMR spectrum consisting of only two singlet signals at δ 7.01 and at 0.45, corresponding to the C_{60}-H and trimethylsilyl protons, respectively. No signals for other regioisomers were observed. The ^{13}C NMR spectrum of **3** exhibited signals for the acetylenic carbons (δ 107.50 and 88.48), sp^3 carbons in the C_{60} core (δ 62.06 and 55.44), and a silylmethyl carbon (δ −0.06), together with 28 signals for the sp^2 carbons of the C_{60} core in the region between δ 151.57 and 135.05. Assuming that two more signals are hidden by incidental overlapping, it is possible that this adduct has C_s symmetry such as structure **3**, which has the ethynyl group and hydrogen added across a 6,6-junction bond of the original C_{60}. The ^1H NMR chemical shift for the methine proton on the C_{60} core (δ 7.01) is considerably deshielded as compared with the corresponding signals in alkyl or phenyl derivatives ($RC_{60}H$), which are in the range of δ 6.04 (R = Me) to δ 6.81 (R = Ph).[3b] This is most probably ascribed to the deshielding effect of the triple bond attached in close proximity.

The UV-vis spectrum of **3** showed a strong resemblance to the spectra of the C_{60} derivatives in which one of the 6,6-junction bonds was saturated by addition reactions,[3b,5] thus supporting the structure **3**.

In order to further confirm the site of protonation of the first formed carbanion of ethynylated C_{60} (**2**), the charge density was estimated by the use of AM1 molecular orbital calculations,[6] exactly as has been done by Hirsch and co-workers for *tert*-butylfullerenyl carbanion.[3a] The carbon with the largest negative charge (−0.29) on the C_{60} surface, i.e., the most probable site of protonation, was found to be the one connected by a 6,6-bond to the ethynylated carbon as in the case of *tert*-butylfullerenyl carbanion.[3a] The carbon with the second largest negative charge (−0.15) was shown to be the one at the position *para* to the ethynylated carbon in the same six-membered ring.

In order to examine the generality of the present method for ethynylation of C_{60}, addition of phenylethynyllithium was conducted under similar reaction conditions to give the monoadduct, $HC_{60}(C{\equiv}CC_6H_5)$ (**5**), in 33% yield. The structural identification was made based on ^1H and ^{13}C NMR as well as MS spectral data.

Finally, the redox properties of the newly obtained ethynylfullerenes **3** and **5** were examined by the use of

---

[†] Kyoto University.

[‡] The Hong Kong University of Science and Technology.

(1) For reviews, see Taylor, R.; Walton, D. R. M. *Nature* **1993**, *363*, 685−693. Olah, G. A.; Bucsi, I.; Aniszfeld, R.; Prakash, G. K. S. *Carbon* **1992**, *30*, 1203−1211. Fagan, P. J.; Chase, B.; Calabrese, J. C.; Dixon, D. A.; Harlow, R.; Krusic, P. J.; Matsuzawa, N.; Tebbe, F. N.; Thorn, D. L.; Wasserman, E. *Carbon* **1992**, *30*, 1213−1226. Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 157−161.

(2) A systematic study on redox behaviors of organofullerenes has been reported: Suzuki, T.; Maruyama, Y.; Alasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, *116*, 1359−1363.

(3) (a) Hirsch, A.; Soi, A.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 766−768. (b) Hirsch, A.; Grösser, T.; Skiebe, A.; Soi, A. *Chem. Ber.* **1993**, *126*, 1061−1067. (c) Fagan, P. J.; Krusic, P. J.; Evans, D. H.; Lerke, S. A.; Johnston, E. *J. Am. Chem. Soc.* **1992**, *114*, 9697−9699.

(4) Multiple addition of these reagents was reported earlier by Wudl et al., but the products were identified mostly by mass spectral data: Wudl, F.; Hirsch, A.; Khemani, K. C.; Suzuki, T.; Allemand, P.-M.; Koch, A.; Eckert, H.; Srdanov, G.; Webb, H. M. In *Fullerenes Synthesis, Properties, and Chemistry of Large Carbon Clusters*; Hammond, G. S., Kuck, V. J. Eds.; ACS Symposium Series 48, American Chemical Society: Washington, DC, 1992, pp 161−175.

(5) For example: (a) An, Y.-Z.; Anderson, J. L.; Rubin, Y. *J. Org. Chem.* **1993**, *58*, 4799−4801 and the references cited therein. (b) 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*, 5829−5830. (c) Komatsu, K.; Kagayama, A.; Murata, Y.; Sugita, N.; Kobayashi, K.; Nagase, S.; Wan, T. S. M. *Chem. Lett.* **1993**, 2163−2166.

(6) The calculations were conducted using the standard method implemented in the MOPAC 6.0 semiempirical orbital package.

0022-3263/94/1959-6101$04.50/0

Table 1. Results of Cyclic Voltammetry[a]

compd	E_{ox} irrev peak potl	reversible, $E_{1/2}$[b]			
		E_{red}^1	E_{red}^2	E_{red}^3	E_{red}^4
C_{60}	+1.41	−0.93 (88)	−1.36 (95)	−1.85 (95)	−2.35 (107)
3	+1.43	−1.02 (105)	−1.42 (94)	−1.95 (103)	−2.43 (96)
5	+1.44	−0.97 (100)	−1.39 (103)	−1.81 (85)	−2.33 (117)

[a] Potential in volts vs ferrocene/ferrocenium measured in benzonitrile with tetrabutylammonium tetrafluoroborate (0.05 M) as a supporting electrolyte; scan rate, 0.1 V s^{-1}. [b] $E_{pa} - E_{pc}$ values in millivolts are shown in parentheses.

cyclic voltammetry in benzonitrile. The voltammograms exhibited one irreversible oxidation peak and four reversible reduction waves as in the case of C_{60} itself. The results are shown in Table 1. In spite of the general tendency that cathodic shifts of reduction potentials result from the saturation of one of the π-bonds on the C_{60} surface by addition of a carbonaceous group,[2,5c] the reduction potentials of phenylethynyl derivative **5** were not much different from those of C_{60} itself. This could be attributed to the electron-withdrawing inductive effect of the phenylethynyl group,[7] which canceled out the expected cathodic shift mentioned above. On the other hand, the reduction potentials of **3** were generally more negative by ≤0.1 V, reflecting the electropositivity of the silyl group.

The present method, i.e. the nucleophilic addition under forced conditions, is considered to have general applicability for the ethynylation of fullerenes, and further study is now under way to obtain a wide variety of acetylenic fullerenes with unique structures and properties including a dumbbell type dimer, for example.

Experimental Section

NMR spectra were at 300 MHz for ^1H and 75 MHz for ^{13}C NMR. Cyclic voltammetry was conducted using a three-electrode cell with a glassy carbon working electrode, a platinum counter electrode, and a Ag/0.01 M $AgNO_3$ reference electrode. The potential was corrected against ferrocene used as an internal standard. All the TLC analyses were conducted with hexane/silica gel 60 F-254 (Merck). C_{60} was separated from a commercial $C_{60}-C_{70}$ mixture (92:8 by weight; MER Co.) by the use of a Norit carbon–silica gel column.[8] THF was freshly distilled from sodium benzophenone ketyl before use. Toluene and benzonitrile were distilled from Na and P_2O_5, respectively. Reactions were conducted under an argon atmosphere in predried glassware.

[(Trimethylsilyl)ethynyl]hydrofullerene (3). A solution of [(trimethylsilyl)ethynyl]lithium (**2**) was prepared by adding 0.32 mL (0.49 mmol) of 1.54 N BuLi in hexane to a stirred solution of (trimethylsilyl)acetylene (0.071 mL, 49 mg, 0.50 mmol) in 0.7 mL of THF at −78 °C and stirring the mixture at 0 °C for 0.5 h. To a vigorously stirred solution of C_{60} (36.3 mg, 0.0504 mmol) in refluxing toluene (20 mL), was added a solution of **2** dropwise via syringe. After a total of 0.6 mL (0.22 mmol) of the solution of **2** was added over 2 min, a black suspension resulted. After cooling to rt, the mixture was treated with CF_3CO_2H (0.2 mL, 2.6 mmol) to give a dark brown solution, which was then evaporated under vacuum. The residual solid was extracted with toluene (10 mL × 3), and the crude product was separated by medium-pressure liquid chromatography on silica gel 60 (Merck) eluting with hexane. From the first fractions was obtained unchanged C_{60} (5.5 mg, 15%); TLC R_f 0.70. From the second fraction was isolated **3** (18.7 mg, 45%) as a dark brown powder: mp > 300 °C; TLC R_f 0.53; ^1H NMR ($CDCl_3-CS_2$ (1:1)) δ 7.01 (s, 1 H, $C_{60}H$), 0.45 (s, 9 H, $SiCH_3$); ^{13}C NMR ($CS_2-(CD_3)_2CO$ (4:1)) δ 151.57, 151.26, 147.52, 147.25, 146.70, 146.35, 146.31, 146.16, 145.76, 145.63, 145.42, 145.38, 145.30, 144.65, 144.45, 143.17, 143.00, 142.58, 142.54, 142.08, 142.01, 141.98, 141.81, 141.64, 141.57, 140.31, 135.96, 135.05 (28 signals, sp^2-carbons in the C_{60} core), 107.50 ($C{\equiv}CSi$), 88.48 ($C{\equiv}CSi$), 62.06 (CH in the C_{60} core), 55.44 (quaternary sp^3-C in the C_{60} core), −0.06 ($SiCH_3$); UV-vis (cyclohexane) λ_{max} (log ϵ) 213 nm (5.09), 256 (5.04), 325 (4.54), 431 (3.58), 478sh (3.22), 543sh (2.98), 635 (2.61), 668 (2.36), 689 (2.50), 701 (2.62); FAB MS *m/z* 818 (M^+) and intense peak at 720 (C_{60}). Anal. Calcd for $C_{65}H_{10}Si$: C, 95.34; H, 1.23. Found: C, 94.52; H, 1.36.

The third fraction afforded a mixture of regioisomers of the bisadduct **4** (7.5 mg, 16%) as a dark brown powder: TLC R_f 0.25; ^1H NMR (300 MHz, $CDCl_3-CS_2$ (1:1)) δ 6.94 (s), 6.82 (s), 6.49 (s), 5.97 (s), 0.39 (s), 0.35 (s), 0.31 (s), 0.08 (s), 0.04 (s); FAB MS *m/z* 916 (M^+), 818 ($M^+ - HC{\equiv}CSi(CH_3)_3$), and intense peak at 720 (C_{60}).

(Phenylethynyl)hydrofullerene (5). Similarly, 0.45 mL (0.21 mmol) of a 0.46 M THF solution of (phenylethynyl)lithium, prepared in the same way as described above, was added dropwise to a stirred and refluxed solution of C_{60} (50.6 mg, 0.0702 mmol) in toluene (30 mL) over 3 min. After 1 min, the resulting black suspension was treated with excess CF_3CO_2H, worked up in the same way as above, and chromatographed to give unchanged C_{60} (7.3 mg, 14%) and monoadduct **5** (19.2 mg, 33.2%) as a dark brown powder: mp > 300 °C; TLC R_f 0.48; ^1H NMR ($CDCl_3-CS_2$ (1:1)) δ 7.77 (m, 2 H, *o*-H), 7.45 (m, 3 H, *m,p*-H), 7.13 (s, 1 H, $C_{60}H$) (δ in $CS_2-(CD_3)_2CO$ (4:1), 7.73, 7.44, and 7.18); ^{13}C NMR ($CS_2-(CD_3)_2CO$ (4:1)) δ 151.51, 151.22, 147.49, 147.21, 146.63, 146.30, 146.27, 146.12, 145.70, 145.60, 145.55, 145.41, 145.33, 145.25, 144.61, 144.42, 143.13, 142.52, 142.49, 142.06, 141.97, 141.93, 141.81, 141.62, 141.54, 140.30, 140.27, 135.99, 135.08 (29 signals, sp^2-carbons in the C_{60} core), 132.06, 128.91, 128.55 (three signals, CH in the phenyl group), 122.47 (ipso-C in the phenyl group), 92.24 ($C{\equiv}CPh$), 84.05 ($C{\equiv}C$-Ph), 61.87 (CH in the C_{60} core), 55.03 (quaternary sp^3-C in the C_{60} core); UV-vis (cyclohexane) λ_{max} 209 nm (log ϵ 5.09), 257 (5.08), 329 (4.53), 405 (3.57), 432 (3.41), 483sh (3.07), 543sh (2.94), 599 (2.76), 667 (2.33), 689 (2.43), 701 (2.53); FAB MS *m/z* (822, M^+) and intense peak at 720 (C_{60}). Anal. Calcd for $C_{68}H_6$: C, 99.27; H, 0.73. Found: C, 98.47; H, 0.75.

Acknowledgment. This work was supported by Grant-in-Aid for Scientific Research on Priority Areas (No. 05233220) from the Ministry of Education, Science and Culture, Japan. Calculations were conducted at the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University.

Supplementary Material Available: The ^1H NMR, ^{13}C NMR, and UV-vis spectra of **3** and **5**, cyclic voltammograms of C_{60}, **3**, and **5**, and charge densities of carbanion **2** and some bond lengths of **3** calculated by AM1 (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(7) The importance of the inductive effect of attached organic groups on the redox properties of C_{60} derivatives has been clarified (ref 2). As an index of the inductive effect of the phenylethynyl group, both the substituent constants σ_m and σ_I have been estimated as 0.29: Charton, M. In *Progress in Physical Organic Chemistry*; Taft, R. W., Ed.; Wiley: New York, 1981; Vol. 13, pp 119–251.

(8) Scrivens, W. A.; Bedworth, P. V.; Tour, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 7917–7919.