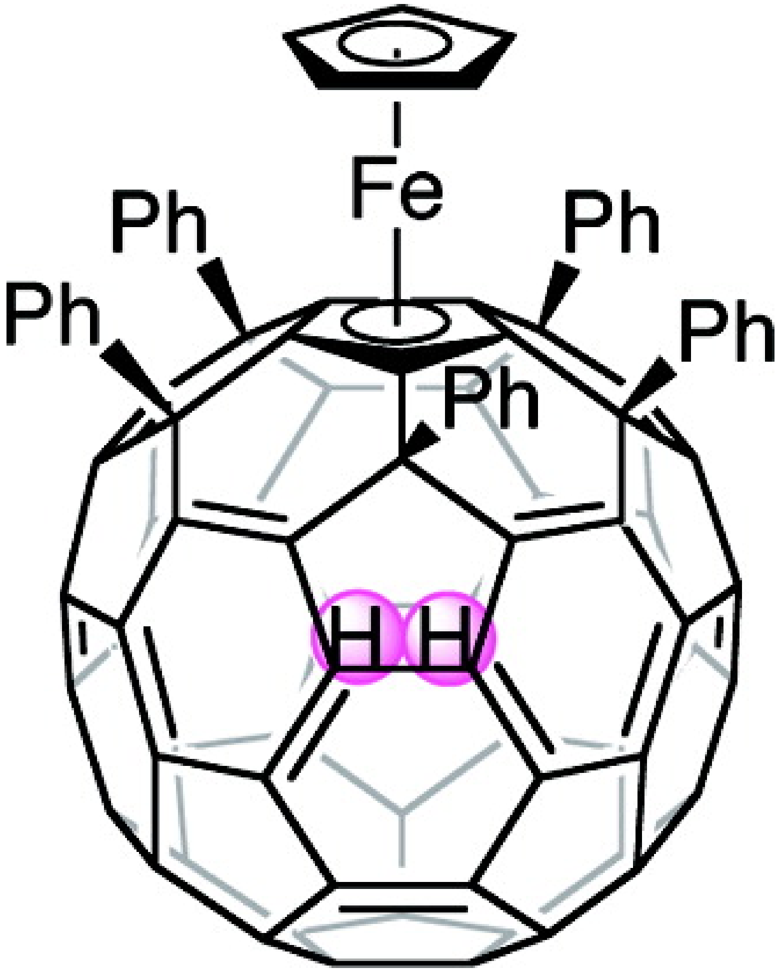
Communication

Organic and Organometallic Derivatives of Dihydrogen-Encapsulated [60]Fullerene

Yutaka Matsuo, Hiroyuki Isobe, Takatsugu Tanaka, Yasujiro
Murata, Michihisa Murata, Koichi Komatsu, and Eiichi Nakamura

J. Am. Chem. Soc., **2005**, 127 (49), 17148-17149• DOI: 10.1021/ja056077a • Publication Date (Web): 18 November 2005



More About This Article

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Organic and Organometallic Derivatives of Dihydrogen-Encapsulated [60]Fullerene

Yutaka Matsuo,[‡] Hiroyuki Isobe,[⊥] Takatsugu Tanaka,[⊥] Yasujiro Murata,[§] Michihisa Murata,[§]
Koichi Komatsu,[§] and Eiichi Nakamura*[,‡,⊥]

*Nakamura Functional Carbon Cluster Project, ERATO, Japan Science and Technology Agency and
Department of Chemistry, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan, and
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*

Received September 2, 2005; E-mail: nakamura@chem.s.u-tokyo.ac.jp

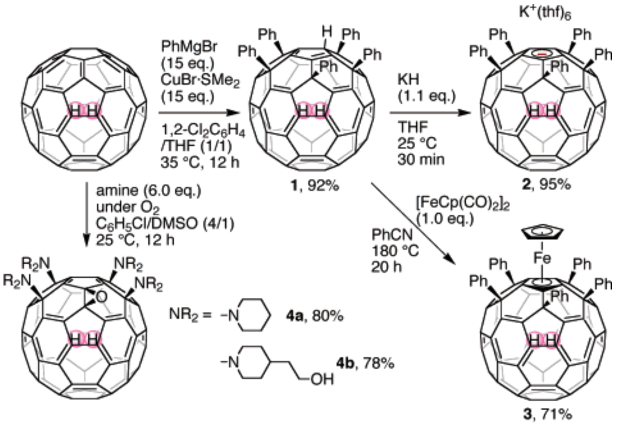
The dihydrogen-encapsulated [60]fullerene, $H_2@C_{60}$[1] is unique, among other atom- or molecule-encapsulated fullerenes, in that it has been synthesized rationally from C_{60} through “molecular surgery” method[2] on a gram scale with maximum 100% H_2 incorporation. This makes the molecule an attractive target of further studies on its properties and applications. Herein we report the first syntheses and X-ray structures of organic and organometallic derivatives of $H_2@C_{60}$ and the use of the encapsulated molecular hydrogen as a magnetic shielding probe.

Regioselective penta-addition of organocopper compounds[3] to [60]fullerene has created a variety of $R_5C_{60}H$ molecules and has led to the development of new classes of compounds and materials, including fullerene−metallocene hybrid molecules,[4,5] liquid-crystal-forming nano shuttlecocks,[6] and bilayer vesicles.[7] The reaction can be performed easily on a 10-g scale. We therefore became intrigued with how the encapsulated H_2 of the penta-adducts is useful as the magnetic shielding probe. Thus, $H_2@C_{60}$ ($H_2@C_{60}/C_{60} = 4/1$) was treated with 15 equiv of a phenylcopper prepared in situ from equimolar amounts of PhMgBr and $CuBr{\cdot}SMe_2$ under the same conditions as those applied for empty C_{60} (Scheme 1). The reaction afforded the desired product **1** as an orange powder in 92% isolated yield. Compound **1** was characterized by ^1H and ^{13}C NMR measurements and further converted to its potassium and iron complexes.

Deprotonation of **1** by 1.1 equiv of KH in THF at room temperature for 30 min afforded a dark-red solution, from which $[K(thf)_6][H_2@C_{60}Ph_5]$ (**2**) was obtained. We also synthesized the dihydrogen-encapsulated pentaphenyl bucky ferrocene $Fe(H_2@C_{60}Ph_5)C_5H_5$ (**3**) in a manner similar to that applied to the synthesis of empty buckyferrocene.[4] Heating **1** and $[Fe(C_5H_5)(CO)_2]_2$ in benzonitrile at 180 °C for 20 h afforded **3**, which was obtained as air- and moisture-stable red crystals in 71% isolated yield after purification by silica gel column chromatography and recrystallization from a mixture of CS_2 and ethanol.

We also synthesized compounds that are soluble in a variety of solvents including water. Thus, $H_2@C_{60}$ and piperidine were dissolved in a mixture of chlorobenzene and dimethyl sulfoxide (DMSO) in the presence of molecular oxygen to obtain tetrapiperidinofullerene epoxide **4a** in 80% yield.[8] Similarly, the reaction with 4-(2-hydroxyethyl)piperidine gave an amphiphilic aminofullerene **4b** in 78% yield. The reaction rates in this and the penta-addition reactions were found to be qualitatively the same as those of the empty fullerene, reflecting that the encapsulation of dihydrogen does not affect the reactivity of the fullerene cage as expected.

Scheme 1. Synthesis of Organometallic and Water-Soluble Derivatives of $H_2@C_{60}$ by Regioselective Multifunctionalization Reactions



The structures of the above products were determined by X-ray crystallographic analysis for **2** and **3**. Single crystals of **2** were obtained by slow diffusion of hexane into a THF solution of **2** under argon atmosphere, and those of **3** by slow diffusion of ethanol into a CS_2 solution of **3**. Diffraction data for both compounds were collected at 143 K under nitrogen gas flow.

The crystal structure of **2** consists of two crystallographically independent ion-pairs, $K(H_2@C_{60}Ph_5)(thf)_3$ (**2a**; Figure 1a) and $[K(thf)_6][H_2@C_{60}Ph_5]$ (**2B**; Figure 1b). Comparison of these structures with those reported for $[K(thf)_n][C_{60}Ph_5]$[9] indicates that the encapsulated dihydrogen does not change either the molecular structures or supramolecular and crystal packing structures.

Differential Fourier ($F_o - F_c$) analysis for the crystals of **2** indicates the presence of hydrogen atoms: There was an electron density peak with a height of 0.31 electrons Å^{-3} in the center of the cage of **2a** and **2b**, whereas there was no such electron density in the empty counterpart $[K(thf)_n][C_{60}Ph_5]$.[9] Full structure solution was performed by placing one hydrogen atom[10] with 1.6 occupancy[11] at the differential Fourier peak in the center of C_{60} and isotropic refinement of the H_2 position. After convergence of least-squares refinement, the electron density of dihydrogen in the fullerene cage was found in PLATON[12] contour F_o maps (see Supporting Information). The center of the dihydrogen molecule is located 0.10 Å downward from the centroid of the 60 carbon atoms of the fullerene skeleton.

The crystal structure of **3** is shown in Figure 1c. A differential Fourier map, obtained after placement of iron and carbon atoms during structure solution, exhibited the strongest electron density peak (0.53 electrons Å^{-3}) at the center of the fullerene cage. Contour F_o maps obtained after fully solving the structure[11] also showed high electron density at the center of the cage. Note that no electron density appears in the cage of the empty bucky ferrocene. The center of the dihydrogen molecule is located 0.20 Å downward from the centroid of the 60 carbon atoms of the fullerene skeleton.

[‡] ERATO, Japan Science and Technology Agency.
[⊥] The University of Tokyo.
[§] Kyoto University.

10.1021/ja056077a CCC: $30.25 © 2005 American Chemical Society

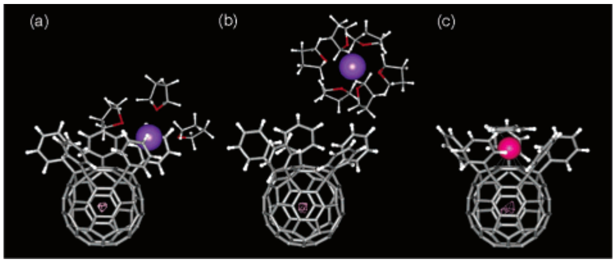


Figure 1. X-ray crystal structures of **2** and **3**. (a) K[H_2@$C_{60}Ph_5$](thf)$_3$ (**2a**). (b) [K(thf)$_6$][H_2@$C_{60}Ph_5$] (**2b**). (c) Fe(H_2@$C_{60}Ph_5$)(C_5H_5) (**3**). Red line-works in the fullerene cages represent differential Fourier peaks.

Table 1. Chemical Shift of Encapsulated H_2 for **1**−**4**

compound	solvent	δ^a
H_2@C_{60}	1,2-$Cl_2C_6D_4$	-1.44^b
1	$CDCl_3/CS_2$	−10.39
2	THF-d_8	−9.79
3	$CDCl_3/CS_2$	−10.44
4a	$CDCl_3$	−10.77
4b	THF-d_8	−10.74
4b	DMSO-d_6/toluene-d_8^c	−10.76
4b	DMSO-d_6	−10.80
4b	D_2O/DMSO-d_6^c	−10.85

[a] The spectra were referenced internally to tetramethylsilane as a standard. [b] Reference 1. [c] Two solvents are mixed at 1:1 ratio (v/v).

As in the He@C_{60},[13] the ^1H NMR chemical shift of the encapsulated H_2 molecule serves as a sensing probe for investigation of the magnetic and electronic properties of the fullerene π-conjugated system (cf. Table 1). The ^1H NMR signals due to the cyclopentadiene of **1** ($\delta = 5.29$) and the phenyl protons remain the same as those of $C_{60}Ph_5H$ (cyclopentadiene; $\delta = 5.30$). The singlet signal of the encapsulated H_2 of **1** appears at $\delta = -10.39$ (Table 1) as opposed to $\delta = -1.44$ for H_2@C_{60}.[1] This extraordinary upfield shift ($\Delta\delta$ 8.95 ppm)[14] indicates that the penta-addition causes a major change in the shielding/deshielding currents, either increased shielding or reduced deshielding effect; the phenylation reaction destroys six deshielding [5]radialene moieties[15] out of the total of 12 in [60]fullerene, but only five shielding cyclohexatriene moieties[15] out of the total of 20. Therefore, the overall outcome of these structural changes must result in strong shielding of the center of the cage. A similar upfield shift was observed with amino-fullerenes **4a** and **b** that have the same number of [5]radialene and cyclohexatriene moieties.[16]

The ^1H NMR measurement of the potassium cyclopentadienide **2** in THF-d_8 indicates a time-averaged C_{5v} symmetric structure. The signal due to the encapsulated H_2 appears as a singlet at $\delta = -9.79$, which is 0.6 ppm lower than **1**, despite the formation of a 6π-electron shielding cyclopentadienide. Signals due to the phenyl groups of **2** appeared at essentially the same magnetic field as in the empty [K(thf)$_6$][$C_{60}Ph_5$].[3] The ^{13}C NMR spectra of **1** and **2** were essentially the same as those of the empty counterparts.

It is interesting to note that the ^1H NMR chemical shift of the diydrogen in the potassium cyclopentadienide **2** ($\delta = -9.79$) is the most deshielded among all related compounds in Table 1. While it is difficult to rationalize the origin of this deshielding, we may tentatively ascribe this to the location of the dihydrogen relative to the anionic 6π-cyclopentadienide moiety in **2**; that is, one of the hydrogen atoms may be located in a deshielding region of the cage.[17] Further experimentation is necessary to discuss this issue in detail.

The amphiphilic aminofullerene **4b** can be dissolved in a variety of solvents, which allowed us to study solvent effects on the ^1H NMR chemical shift of the encapsulated H_2 (Table 1). Its signal was observed as a singlet at −10.74, −10.76, −10.80, and −10.85 ppm in THF-d_8, DMSO-d_6/toluene-d_8, DMSO-d_6, and D_2O/DMSO-d_6, respectively. The upfield shifting of the encapsulated H_2 follows qualitatively the magnetic susceptibility of the solvents,[18] suggesting that a nonspecific solvent effect contributes to the change in chemical shifts.[19]

In summary, we have synthesized the organic and organometallic derivatives of dihydrogen-encapsulated [60]fullerene **2**−**4** in good yield and showed that the uniquely upfield-shifted singlet signal of the encapsulated dihydrogen can act as a sensitive probe for inside and outside environment of the fullerene cage. With the success of the multi-addition reactions in hand, we expect that a number of other reactions known for fullerenes can be performed readily on H_2@C_{60} and will produce an array of new compounds for further studies.

Acknowledgment. We thank Monbukagakusho (the 21st Century COE Program for Frontiers in Fundamental Chemistry and grant-in-aid for Scientific Research, Young Scientists (A)) for partial financial support.

Supporting Information Available: Synthetic procedures and spectral data (PDF) of the new compounds as well as CIF files for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Komatsu, K.; Murata, M.; Murata, Y. *Science* **2005**, *307*, 238−240.
(2) (a) Rubin, Y. *Top. Curr. Chem.* **1999**, *199*, 67−91. (b) Rubin, Y.; Jarrosson, T.; Wang, G.-W.; Bartberger, M. D.; Houk, K. N.; Schick, G.; Saunders: M.; Cross, R. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1543−1546. (c) Murata, Y.; Murata, M.; Komatsu, K. *J. Am. Chem. Soc.* **2003**, *125*, 7152−7153.
(3) Sawamura, M.; Iikura, H.; Nakamura, E. *J. Am. Chem. Soc.* **1996**, *118*, 12850−12851.
(4) (a) Sawamura, M.; Kuninobu, Y.; Toganoh, M.; Matsuo, Y.; Yamanaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **2002**, *124*, 9354−9355. (b) Herber, R. H.; Nowik, I.; Matsuo, Y.; Toganoh, M.; Kuninobu, Y.; Nakamura, E. *Inorg. Chem.* **2005**, *44*, 5629−5635.
(5) Nakamura, E. *J. Organomet. Chem.* **2004**, *689*, 4630−4635.
(6) (a) Sawamura, M.; Kawai, K.; Matsuo, Y.; Kanie, K.; Kato, T.; Nakamura, E. *Nature* **2002**, *419*, 702−705. (b) Matsuo, Y.; Muramatsu, A.; Hamasaki, R.; Mizoshita, N.; Kato, T.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 432−433.
(7) (a) Zhou, S.; Burger, C.; Chu, B.; Sawamura, M.; Nagahama, N.; Toganoh, M.; Hackler, U. E.; Isobe, H.; Nakamura, E. *Science* **2001**, *291*, 1944−1947. (b) Nakamura, E.; Isobe, H. *Acc. Chem. Res.* **2003**, *36*, 807−815.
(8) Isobe, H.; Tanaka, T.; Nakanishi, W.; Lemiègre, L.; Nakamura, E. *J. Org. Chem.* **2005**, *70*, 4826−4832.
(9) Matsuo, Y.; Tahara, K.; Nakamura, E. *Chem. Lett.* **2005**, *34*, 1078−1079.
(10) The dihydrogen molecule must be moving in the cage even at the liquid nitrogen temperature, which would make it difficult to determine precisely its location under the conditions we employed.
(11) Since starting materials contain H_2@C_{60} and empty C_{60} in 4:1 ratio, refinement of hydrogen atom is performed with 1.6 occupancy.
(12) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7−13.
(13) (a) Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Mroczkowski, S.; Freedberg, D. I.; Anet, F. A. L. *Nature* **1994**, *367*, 256−258. (b) Saunders, M.; Cross, R. J.; Jiménez-Vázquez, H. A.; Shimshi, R.; Khong, A. *Science* **1996**, *271*, 1693−1697.
(14) Large upfield shift has also been observed for some functionalized He@C_{60}. See Birkett, P. R.; Bühl, M.; Khong, A.; Saunders, M.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2037−2039.
(15) (a) Pasquarello, A.; Schulter, M.; Haddon, R. C. *Science* **1992**, *257*, 1660−1661. (b) Bühl, M.; Hirsch, A. *Chem. Rev.* **2001**, *101*, 1153−1183.
(16) We ascribe the difference of chemical shift of the dihydrogen between $C_{60}Ph_5H$ and aminofullerenes to the effect of the carbon and the nitrogen groups attached to the fullerene cage.
(17) Theoretical calculations (GIAO-SCF/6-31G*//HF/6-31G*) suggest that the shielding effect increases from the center toward the bottom. See Supporting Information.
(18) Molar diamagnetic susceptibilities of the solvents (χM): $H_2O = -12.96 \times 10^6$, DMSO = -43.6×10^6, THF = -50.4×10^6, toluene = -66.52×10^6 cm^3·mol^{-1}, respectively. See Gupta, R. R. *Landolt-Börnstein Numerical Data and Functional Relationship in Science and Technology, New Series, II/16, Diamagnetic Susceptibility*; Springer: Berlin, 1986. Takahashi, F.; Sakai, Y.; Nakazawa, Y.; Mizutani, Y. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2967−2971.
(19) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; Wiley: Weinheim, 2003.

JA056077A