

Electron Microscopic Imaging of a Single Group 8 Metal Atom Catalyzing C–C Bond Reorganization of Fullerenes

Eiichi Nakamura,^{*,†} Masanori Koshino,[‡] Takeshi Saito,[‡] Yoshiko Niimi,[‡] Kazu Suenaga,[‡] and Yutaka Matsuo[†]

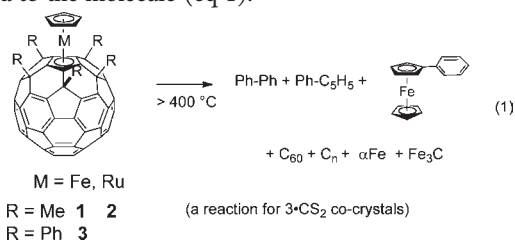
[†]Department of Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

[‡]Nanotube Research Center, National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba 305-8565, Japan

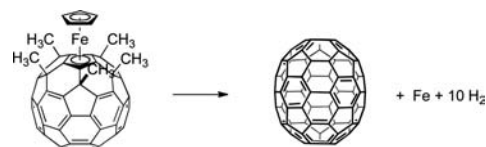
S Supporting Information

ABSTRACT: Heating a bulk sample of [60]fullerene complexes, $(\eta^5\text{-C}_5\text{H}_5)\text{MC}_{60}\text{R}_5$ ($\text{M} = \text{Fe}, \text{Ru}$, $\text{R} = \text{Me}, \text{Ph}$), produces small hydrocarbons because of coupling of R and C_5H_5 via $\text{C}-\text{C}$ and $\text{C}-\text{H}$ bond activation. Upon observation by transmission electron microscopy, these complexes, encapsulated in single-walled carbon nanotubes, underwent $\text{C}-\text{C}$ bond reorganization reactions to form new $\text{C}-\text{C}$ bond networks, including a structure reminiscent of [70]fullerene. Quantitative comparison of the electron dose required to effect the $\text{C}-\text{C}$ bond reorganization of fullerenes and organofullerenes in the presence of a single atom of Ru , Fe , or Ln and in the absence of metal atoms indicated high catalytic activity of Ru and Fe atoms, as opposed to no catalytic activity of Ln . Organic molecules such as hydrocarbons and amides as well as pristine [60]fullerene maintain their structural integrity upon irradiation by ca. 100 times higher electron dose compared to the Ru and Fe organometallics. The results not only represent a rare example of direct observation of a single-metal catalysis but also have implications for the use of single metal atom catalysis in Group 8 metal heterogeneous catalysis.

Group 8 metals have long been known for their unique capability of cleaving $\text{C}-\text{C}$ and $\text{C}-\text{H}$ bonds¹ to create new $\text{C}-\text{C}$ bond networks. Important examples include heterogeneous catalysis such as the Fischer–Tropsch (FT) synthesis,^{2–5} which may accompany the formation of carbon materials.⁶ The latter reaction has relevance to the synthesis of carbon nanotubes (CNTs) and graphene sheets.⁷ The catalytic mechanism has long been the subject of controversy.^{8–11} Although a multimetallic mechanistic scheme for the FT synthesis has frequently been discussed,¹² a recurring question is whether the reaction can occur at a single-metal site.^{13,14} We recently found the thermal conversion of bucky-metalloenes (**1–3**) to carbon materials as well as to volatile compounds that formed through coupling of the organic groups attached to the molecule (eq 1).¹⁵



Scheme 1. Hypothetical Conversion of **1** to [70]Fullerene



This observation prompted us to study whether a single iron or ruthenium atom catalyzes such $\text{C}-\text{C}$ bond reorganization at a single-molecule level. We report herein that, as studied in situ with a series of images obtained by high-resolution transmission electron microscopy (TEM),¹⁶ single molecules of bucky-ferrocene **1**¹⁷ and -ruthenocene **2**,¹⁸ encapsulated tightly in a single-walled CNT, undergo $\text{C}-\text{C}$ bond reorganization reactions under the catalytic effect of a single Group 8 metal atom, without which such reactions require a much larger electron dose.¹⁹ The movie image of a reaction obtained in this study led us to imagine a hypothetical chemical equation: $\text{C}_{60}(\text{CH}_3)_5(\eta^5\text{-C}_5\text{H}_5)\text{M} \rightarrow \text{C}_{70} + 10\text{H}_2 + \text{M}$ (Scheme 1), driven by the release of the strain energy of [60]fullerene and coupling of the feedstock organic groups.

We encapsulated **1** and **2** in an open-ended single-walled CNT ($d = 2.0 \pm 0.3$ nm, similar to the longitudinal length of **1** and **2**)²⁰ under reduced pressure (10^{-4} Pa) at 583–613 K. The tight (peapod) packing of many molecules of **1** in the CNT created a compartment structure (Figures 1 and 2) that prevented migration of the iron atom ($d = 0.3$ nm) from one place to another, ensuring that we studied the activity of a single metal atom without forming multimetallic clusters or carbide that we can detect by TEM.²¹

The TEM movie images of the specimens placed on a sample stage at 293 K were taken on a TEM instrument operating at $E = 120$ kV (dose rate = $(3.5\text{--}3.7) \times 10^4$ e^-/nm^2 frame, 0.23 nm resolution), and also on a 4 K stage on a cryo-TEM instrument equipped with an aberration corrector ($E = 120$ kV, dose rate = 1.5×10^5 e^-/nm^2 frame, $\text{Cs} = 10$ μm , 0.14 nm resolution). A series of TEM images was obtained at a time interval of 2.0–2.1 s (an electron irradiation time of 0.5 s, followed by a non-irradiated image readout time of 1.5–1.6 s).¹⁶

First, we describe the observed catalytic effect of Group 8 elements as studied on a 293 K sample stage at $E = 120$ kV. Ferrocene **1** and ruthenocene **2** start to decompose visually at an electron dose slightly larger than 3.7×10^4 e^-/nm^2 and undergo rapid $\text{C}-\text{C}$ bond reorganization at a dose larger than 2.2×10^5

Received: April 8, 2011

Published: August 22, 2011

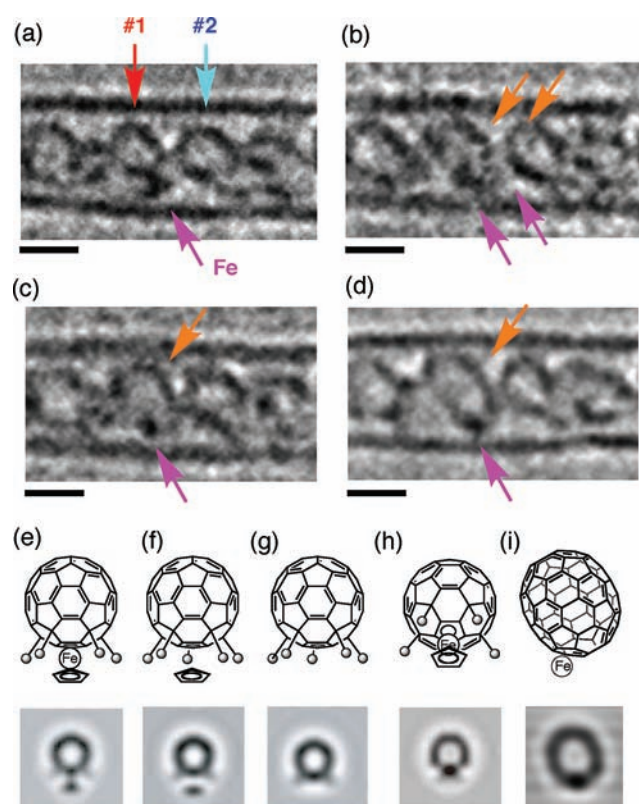


Figure 1. Representative TEM images (out of a total of 19 images collected) of the structure and the reaction of two molecules (#1 and #2) of $\text{Fe}(\text{C}_{60}\text{Me}_3)\text{Cp}$ (**1**) in a single-walled CNT. (a–d) TEM images taken at (a) 3.7×10^4 , (b) 2.2×10^5 , (c) 3.0×10^5 , and (d) 1.6×10^6 electrons/ nm^2 of accumulated electron dose on a 293 K sample stage. Scale bars represent 1 nm. (e) Molecular model and TEM simulation of **1** viewed from the side. Gray balls = CH_3 . (f) Model of **1** lacking the iron atom. (g) Model of **1** lacking the iron atom and the Cp group. (h) **1** as viewed from the top side. (i) [70]Fullerene complexed with an iron atom on the surface.

e^-/nm^2 to form ellipsoidal substances (cf. Figure 1). On the other hand, as we reported earlier, [60]fullerene,²² alkyl carboranes,^{16,23} and amides^{24,25} retain their structural integrity up to an electron dose of well over 10^6 e^-/nm^2 . For instance, [60]fullerene starts to fuse with a neighboring fullerene molecule at a dose of 0.9×10^7 e^-/nm^2 .²² $\text{La}@\text{C}_{82}$ and $\text{Er}@\text{C}_{82}$ are stable also up to a 10^7 e^-/nm^2 electron dose (Table S2).²² Beyond this dose, the metal atom simply leaves the cage and does not speed up C–C bond reorganization. Thus, ruthenium and iron atoms are active catalysts, and f-block transition metals are far less active or not active at all.²⁶

We next describe in detail an example of the image of single bucky-ferrocene molecules **1** and their reaction. We carefully analyzed 25 molecules (Figures 1 and 2) and found that they react via several different pathways.²⁷ The TEM image of a molecule (#1) obtained on a 293 K sample stage, indicated by a red arrow in Figure 1a, looks like **1**. Indeed, this image matches very well with the TEM simulation of **1** as viewed from the side (Figure 1e, Figure S1). Note that the comparison among the TEM simulations of **1**, **1** without iron, and **1** without iron and cyclopentadiene (Cp) (Figure 1e–g) indicates that suitable TEM conditions allow us to visualize the single Fe atom in **1**.

Figure 1a–d illustrates one reaction pathway (which is much better illustrated by the corresponding Movie S1 in the Supporting

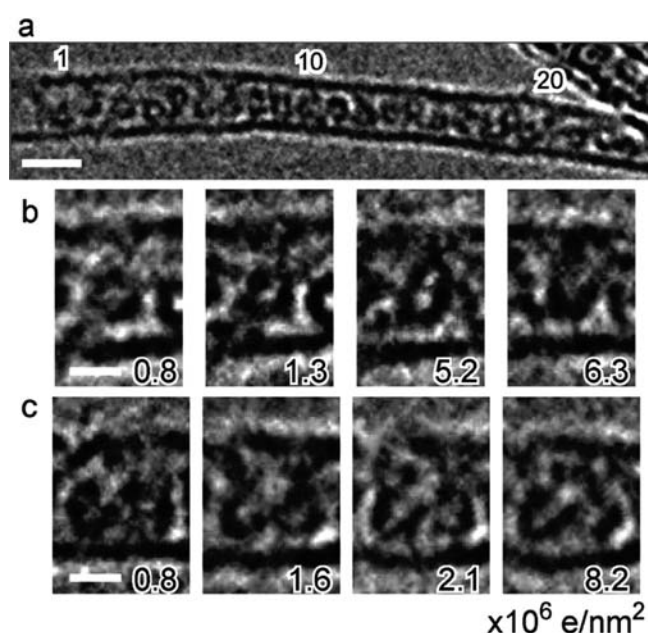


Figure 2. Images of $\text{Fe}(\text{C}_{60}\text{Me}_3)\text{Cp}$ (**1**) in a single-walled CNT and their reactions observed at 4 K with a TEM instrument equipped with an aberration corrector. (a) Twenty-three molecules are aligned one-dimensionally along the tube axis, recorded at 7.5×10^5 electrons/ nm^2 . Each molecule is numbered from left to right, 1–23. The scale bar represents 5 nm. (b,c) The courses of the chemical reactions: (b) intramolecular reaction of molecule 3, leading to the formation of a [70]fullerene-like entity, and (c) bimolecular fusion (bond reorganization involving multiple C–C s-bonds) of two fullerenes 6 and 7. Five continuous images are averaged and shown with their recorded electron doses at the bottom. The scale bars represent 1 nm. See Supporting Information for the corresponding movie images.

Information). The clearly visible molecular image of molecule #1 in Figure 1a, obtained by the first electron dose of 3.7×10^4 e^-/nm^2 , has already eroded by Figure 1b. The most notable change here is the disappearance of the [60]fullerene's spherical image and the growth of an ellipsoidal structure (Figure 1b, orange arrow) reminiscent of a half of [70]fullerene on the side facing molecule #2 (to be compared with the model of a [70]fullerene/Fe complex in Figure 1i). The new structure was observed in Figure 1b–d and further on, suggesting that it is a stable structure, possibly possessing an aromatic C–C network. Given the bulk experimental result in eq 1 and the tight peapod packing that prevents migration of molecules and atoms among the cavities of the peapod compartments, we consider that this new structure has grown intramolecularly out of the [60]fullerene cage and the CH_3 and Cp groups catalyzed by the iron atom that originally constituted a part of **1**.

The iron atom, indicated by a purple arrow, moved slightly from the original position in Figure 1a to a different position in Figure 1d, where the iron atom may be simply attached to the carbon network (i.e., Figure 1i) or incorporated in the C–C network.²¹ The difference pertains to the well-known ability of d-block transition metals to bind tightly to carbon π -systems^{28–30} and to the lack of such ability of the alkali metals. The formation of a similar [70]fullerene-like image (Movie S2) was observed for the reaction of ruthenocene **2**, which had already started to decompose in the first image (Figure S2).

Another molecule (#2), indicated by a blue arrow in Figure 1a (to be compared with the molecular model and TEM simulation

in Figure 1h), appears to retain the [60]fullerene core through Figure 1a–d. The formation of [60]fullerene was observed in the bulk experiment for 3 (eq 1).

As observed on a 4 K sample stage, the reaction slowed down, requiring a higher electron dose ($>9.3 \times 10^6 \text{ e}^-/\text{nm}^2$) to allow about 70% of 23 molecules to undergo C–C bond reorganization (Figure 2a taken at an accumulated dose of $7.5 \times 10^5 \text{ e}^-/\text{nm}^2$; for the semistatistic analysis of reaction pathways, see Table S1; see Movie S3 for the original movie from which Figure 2 was prepared). The 4 conditions therefore allowed us to compare the reactivities of many molecules at the same time. The molecules numbered 1–23 from left to right were tightly packed side-by-side with random spatial orientations. This randomness is fortunate because it allowed us to study the structure and the reactions of several molecules (e.g., 3, 6, and 7). In addition, the observed images showed that the iron atoms neither move drastically from one molecule to another nor form large metal clusters. Several molecules are discussed below in some detail.

Molecule 3 (Figure 2b) remained unchanged for the first two frames (taken at an accumulated electron dose of $1.3 \times 10^6 \text{ e}^-/\text{nm}^2$) but by the third image had grown into a fullerene-like entity larger than [60]fullerene. Figure 2c shows that molecules 6 and 7 quickly decomposed (the second image) and partly fused together to form a larger carbon cage (the fourth image). Parenthetically, we found that the rates of the unimolecular and bimolecular transformations are not dramatically different, because entropy plays little role here, where the molecules are tightly encapsulated in a CNT.

In summary, we have described a unique example of the investigation of metal catalysis at a single-atom level, in which we studied visually C–C bond reorganization reactions catalyzed by a Group 8 metal atom under TEM conditions. In view of such reactivities of Group 8 metals with fullerenes and CNTs, we surmise that the frequently observed, irregular bulges³¹ and defects in CNTs can be formed by single-metal-catalyzed C–C bond formation or cleavage reactions at the local sites after the CNT structure is formed. Identification of the single metal atoms at such sites and determination of the precise reaction mechanism, however, exceed the limit of the presently available instruments. The present observations have offered additional implications on new directions of the use of atomic resolution TEM movies in chemistry: the stability of organic molecules in the absence of catalytic metals will allow us to study structures and reactions of organic and organometallic molecules,^{24,25} the detection of the motion of a single metal atom will be useful in catalysis research, and the movie images of atoms and molecules will contribute to chemistry education in schools.

■ ASSOCIATED CONTENT

Supporting Information. TEM images and movies S1–S3 for observation of bucky-metalloenes and their reactions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

nakamura@chem.s.u-tokyo.ac.jp

■ ACKNOWLEDGMENT

This study was partially supported by KAKENHI (22000008), the Global COE Program, “Chemistry Innovation through

Cooperation of Science and Engineering”, MEXT, Japan, and Nakamura Functional Carbon Cluster Project, ERATO from Japan Science and Technology Agency (JST).

■ REFERENCES

- (1) Nakamura, E.; Yoshikai, N. *J. Org. Chem.* **2010**, *75*, 6061–6067.
- (2) Fischer, F.; Tropsch, H. *Brennst. Chem.* **1923**, *4*, 276–285.
- (3) Adesina, A. A. *Appl. Catal. A: General* **1996**, *138*, 345–367.
- (4) Rostrup-Nielsen, J. R.; Sehested, J.; Nørskov, J. K. *Adv. Catal.* **2002**, *47*, 65–139.
- (5) Davis, B. H. *Fuel Process. Technol.* **2001**, *71*, 157–166.
- (6) Nolan, P. E.; Lynch, D. C.; Cutler, A. H. *J. Phys. Chem. B* **1998**, *102*, 4165–4175.
- (7) Hata, K.; Futaba, D. N.; Mizuno, K.; Namai, T.; Yumura, M.; Iijima, S. *Science* **2004**, *306*, 1362–1364.
- (8) Ekstrom, A.; Lapszewicz, J. *J. Phys. Chem.* **1984**, *88*, 4577–4580.
- (9) Cheng, J.; Gong, X.-Q.; Hu, P.; Lok, C. M.; Ellis, P.; French, S. *J. Catal.* **2008**, *254*, 285–295.
- (10) Li, X.; Cai, W.; Colombo, L.; Ruoff, R. S. *Nano Lett.* **2009**, *9*, 4268–4272.
- (11) Yoshida, H.; Takeda, S.; Uchiyama, T.; Kohno, H.; Homma, Y. *Nano Lett.* **2008**, *8*, 2082–2086.
- (12) Dry, M. E. *Appl. Catal. A: General* **1996**, *138*, 319–344.
- (13) Inderwildi, O. R.; King, D. A.; Jenkins, S. J. *Phys. Chem. Chem. Phys.* **2009**, *11*, 11110–11112.
- (14) Maitlis, P. M.; Long, H. C.; Quyoum, R.; Turner, M. L.; Wang, Z. Q. *Chem. Commun.* **1996**, 1–8.
- (15) Nakae, T.; Matsuo, Y.; Takagi, M.; Sato, Y.; Suenaga, K.; Nakamura, E. *Chem.–Asian J.* **2009**, *4*, 457–465.
- (16) Koshino, M.; Tanaka, T.; Solin, N.; Suenaga, K.; Isobe, H.; Nakamura, E. *Science* **2007**, *316*, 853.
- (17) Sawamura, M.; Kuninobu, Y.; Toganoh, M.; Matsuo, Y.; Yamanaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **2002**, *124*, 9354–9355.
- (18) Matsuo, Y.; Kuninobu, Y.; Ito, S.; Nakamura, E. *Chem. Lett.* **2004**, *33*, 328–329.
- (19) We avoided the use of the phenyl derivative because the products may be higher boiling and contaminate the TEM column.
- (20) Saito, T.; Xu, W.-C.; Ohshima, S.; Ago, H.; Yumura, M.; Iijima, S. *J. Phys. Chem. B* **2006**, *110*, 5849–5853.
- (21) Shiozawa, H.; Pichler, T.; Grüneis, A.; Pfeiffer, R.; Kuzmany, H.; Liu, Z.; Suenaga, K.; Kataura, H. *Adv. Mater.* **2008**, *20*, 1443–1449.
- (22) Koshino, M.; Niimi, Y.; Nakamura, E.; Kataura, H.; Okazaki, T.; Suenaga, K.; Iijima, S. *Nat. Chem.* **2010**, *2*, 117–124.
- (23) Under the TEM observation, we did not observe expansion of carborane framework that can potentially take place in light of previous studies in solution, cf.: Callahan, K. P.; Evans, W. J.; Lo, F. Y.; Strouse, C. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 296–302.
- (24) Solin, N.; Koshino, M.; Tanaka, T.; Takenaga, S.; Kataura, H.; Isobe, H.; Nakamura, E. *Chem. Lett.* **2007**, *36*, 1208–1209.
- (25) Nakamura, E.; Koshino, M.; Tanaka, T.; Niimi, Y.; Harano, K.; Nakamura, Y.; Isobe, H. *J. Am. Chem. Soc.* **2008**, *130*, 7808–7809.
- (26) Note that the reaction conditions for the present TEM observations in a vacuum are such that the progress of the reaction depends largely on the electron dose²⁴ rather than following various empirical equations known for the temperature dependence of the reaction rate in solution.
- (27) Note that the lack of statistical information inherent to single-molecule imaging rears its head here. The number of specimen molecules is too small to draw any statistical conclusions.
- (28) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233–241.
- (29) Stephens, A. H. H.; Green, M. L. H. *Adv. Inorg. Chem.* **1997**, *44*, 1–43.
- (30) Balch, A. L.; Olmstead, M. M. *Chem. Rev.* **1998**, *98*, 2123–2165.
- (31) Nasibulin, A. G.; Anisimov, A. S.; Pikhitsa, P. V.; Jiang, H.; Brown, D. P.; Choi, M.; Kauppinen, E. I. *Chem. Phys. Lett.* **2007**, *446*, 109–114.