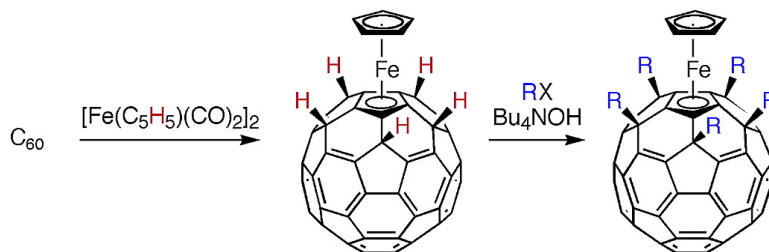


## Synthesis of Ferrocene/Hydrofullerene Hybrid and Functionalized Bucky Ferrocenes

Motoki Toganoh, Yutaka Matsuo, and Eiichi Nakamura

*J. Am. Chem. Soc.*, **2003**, 125 (46), 13974-13975 • DOI: 10.1021/ja037335b • Publication Date (Web): 28 October 2003

Downloaded from <http://pubs.acs.org> on March 30, 2009



### More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 15 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

## Synthesis of Ferrocene/Hydrofullerene Hybrid and Functionalized Bucky Ferrocenes

Motoki Toganoh, Yutaka Matsuo, and Eiichi Nakamura\*

Department of Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

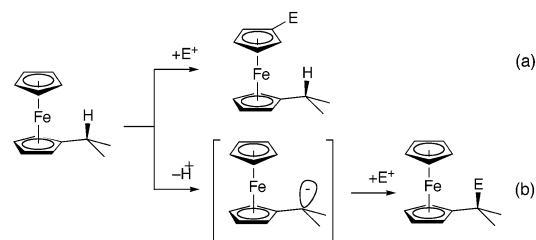
Received July 16, 2003; E-mail: nakamura@chem.s.u-tokyo.ac.jp

Like benzene, ferrocene is amenable to functionalization by direct electrophilic substitution of the  $6\pi$ -cyclopentadienide ring (Scheme 1a).<sup>1</sup> This analogy with benzene may call for the generation of a “benzylic” anion and subsequent trapping with an electrophile  $E^+$  (Scheme 1b), which is difficult, to our knowledge. We report herein that this latter route is possible when the anion is a part of the extensive conjugation of [60]fullerene. For instance, [60]fullerene has been converted first into a ferrocene/hydrofullerene hybrid Fe-(C<sub>60</sub>H<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>) (**1**), and then into a penta-alkylated product Fe-(C<sub>60</sub>R<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>) (**2**) by treatment with methanolic Bu<sub>4</sub>NOH and an excess alkyl halide (Scheme 2). The reaction is applicable to the synthesis of a variety of “bucky ferrocene” derivatives and half-sandwich molecules **8–16** (Chart 1). This synthesis of  $\eta^5$ -fullerene–metal complexes allows the introduction of functionalized groups and hence is complementary to the previous route relying on organocopper reagents.<sup>2</sup>

The new chemistry depends crucially on the synthesis of the hydrofullerene–iron(II) complexes such as **1**, which was made possible according to the hydrometalation protocol that we reported recently.<sup>3</sup> Thus, treatment of [60]fullerene and its derivatives [C<sub>60</sub>-(PhCH<sub>2</sub>)<sub>2</sub> (**3**) and C<sub>60</sub>(PhCH<sub>2</sub>)<sub>2</sub>PhH<sup>5</sup> (**4**)] with [Fe(C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub> in PhCN at 160 °C afforded the desired hydroferrated product in 25–82% yield (Table 1). Contrary to the hydrometalation reaction of fullerene with Re<sub>2</sub>(CO)<sub>10</sub> that utilizes 9,10-dihydroanthracene as a hydrogen source, cyclopentadiene liberated from [Fe(C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub> acts as the hydrogen source in this reaction.<sup>6</sup> The reaction of C<sub>60</sub>(PhCH<sub>2</sub>)<sub>2</sub>PhH (**4**) was particularly clean and requires only a stoichiometric amount of [Fe(C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub> to achieve the 82% yield (Table 1, entry 3; 1 mol of the Fe(I) dimer is required to obtain 1 mol of the Fe(II) product). In the reaction of C<sub>60</sub>(PhCH<sub>2</sub>)<sub>2</sub> we obtained the ferrocene **5** in 44% yield (entry 2), as the reaction was complicated by competitive replacement of a benzyl group with a hydrogen atom. The reaction of [60]fullerene gave **1** in 25% yield (entry 1). The low yield is probably due to poor solubility of fullerene (and also the intermediates) in PhCN. The present procedure allowed the synthesis of a ferrocene/fullerene hybrid bearing substituents on the cyclopentadienide moiety. For instance, a 1,3-bis(trimethylsilyl)cyclopentadienyl ferrocene **7** was synthesized by the reaction of **4** with [Fe(1,3-TMS<sub>2</sub>C<sub>5</sub>H<sub>3</sub>)(CO)<sub>2</sub>]<sub>2</sub> (TMS = Me<sub>3</sub>Si, entry 4).

The hydrofullerene structures were assigned on the basis of spectroscopic analogy with the corresponding hydrometalation products<sup>3</sup> and the ferrocene/fullerene hybrid molecules prepared by the organocopper route<sup>7</sup> (the high-resolution APCI-TOF mass, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra) and the subsequent conversion to the alkylated products as described below. For instance, the <sup>1</sup>H NMR spectrum of **1** shows only two singlets, one due to the cyclopentadienyl protons ( $\delta$  4.94 ppm) and the other due to the protons on fullerene ( $\delta$  5.52 ppm). Only nine signals were observed in the <sup>13</sup>C NMR spectrum (C<sub>5v</sub> symmetry); namely, two signals due to the two cyclopentadienides ( $\delta$  71.11 and 85.32 ppm), one

### Scheme 1



### Scheme 2

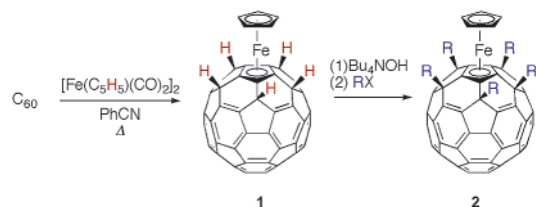
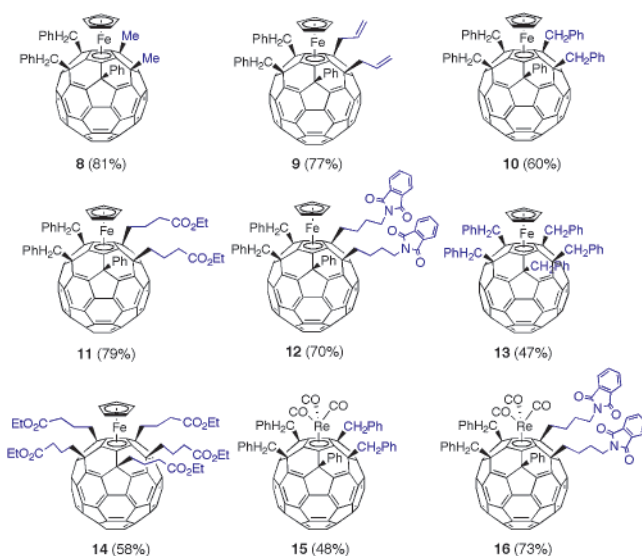


Chart 1. Alkylated [60]Fullerene–Metal Complexes Obtained via Deprotonation/Alkylation Route<sup>a</sup>


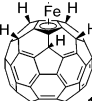
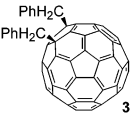
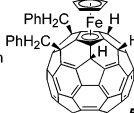


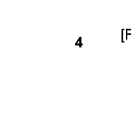
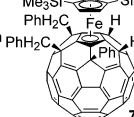


<sup>a</sup> The alkylating agent used in each case is described in the text, and the alkyl groups are colored in blue. Experimental conditions are shown in Supporting Information.

signal due to the H-bearing sp<sup>3</sup> carbon atoms ( $\delta$  45.39 ppm, <sup>1</sup>J<sub>CH</sub> = 143 Hz) and six signals due to the rest of the fullerene sp<sup>2</sup> carbon atoms.

The key finding in the present study is that one can deprotonate the hydrofullerene,<sup>8</sup> and alkylate the resulting anion regioselectively with an alkyl halide (Scheme 2 and Chart 1). After considerable experimentation, methanolic Bu<sub>4</sub>NOH in PhCN was found to be

**Table 1.** Hydroferration of [60]Fullerene Derivatives<sup>a</sup>

Substrate	Reagent	Time	Product	Yield
	$[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2]_2$ (5 eq)	22 h		25%
	$[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2]_2$ (10 eq)	90 h		44%
	$[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2]_2$ (1.0 eq)	14 h		82%
	$[\text{Fe}(\text{C}_5(1,3\text{-TMS})_2\text{H}_3)(\text{CO})_2]_2$ (5 eq)	24 h		53%

<sup>a</sup> See Supporting Information for the experimental conditions.

the best base to achieve the deprotonation/alkylation sequence. For instance, the addition of  $\text{Bu}_4\text{NOH}$  to the ferrocene **6** in  $\text{PhCN-d}_5$  at ambient temperature causes color change from light red to dark red within a few seconds, and  $^1\text{H NMR}$  measurement of the solution showed the disappearance of the two protons attached to the fullerene core (spectrum in Supporting Information). The anion was thermally rather unstable but could be alkylated in good yield with an excess of an alkyl halide (5–40 equiv). Thus, the reaction with methyl iodide completed within 10 min gave the dimethylated compound  $\text{Fe}[\text{C}_{60}(\text{PhCH}_2)_2\text{PhMe}_2](\text{C}_5\text{H}_5)$  (**8**) in 81% isolated yield as a single regioisomer. Similarly the reaction with allyl and benzyl bromide gave  $\text{Fe}[\text{C}_{60}(\text{PhCH}_2)_2\text{Ph}(\text{allyl})_2](\text{C}_5\text{H}_5)$  (**9**) and  $\text{Fe}[\text{C}_{60}(\text{PhCH}_2)_4\text{Ph}](\text{C}_5\text{H}_5)$  (**10**) in 77 and 60% yield, respectively. The reaction conditions are mild enough to allow the reaction with ethyl 4-bromobutanoate and *N*-(4-bromobutyl)phthalimide to give the diester  $\text{Fe}[\text{C}_{60}(\text{PhCH}_2)_2\text{Ph}(\text{EtOOCCH}_2)_2](\text{C}_5\text{H}_5)$  (**11**) in 64% yield and diphthalimide **12** in 70% yield, respectively. When ethyl 4-iodobutanoate (5 equiv) was used instead of the bromide, the product **11** was obtained in 79% yield. Penta-alkylation reaction of the pentahydrofullerene **1** also gave the desired products **13** and **14** in 47 and 58% yield, respectively. Starting with [60]fullerene, the overall yield of the two-step synthesis of **13** that includes formation of no fewer than 11 covalent bonds was a 12% yield.

The present alkylation conditions can be applied also to a rhenium complex: the deprotonation/alkylation of  $\text{Re}[\text{C}_{60}(\text{PhCH}_2)_2\text{PhH}_2](\text{CO})_3$  afforded the expected product  $\text{Re}[\text{C}_{60}(\text{PhCH}_2)_4\text{Ph}](\text{CO})_3$  (**15**) and  $\text{Re}[\text{C}_{60}(\text{PhCH}_2)_2\text{Ph}(\text{C}_6\text{H}_4(\text{CO})_2\text{NC}_4\text{H}_8)_2](\text{CO})_3$  (**16**) in 48 and 73% yield, respectively. In all cases of the alkylation reactions, we observed neither over-alkylated products nor regioisomers of the desired alkylation product. The structure of the alkylation products was determined by spectroscopic data, which were similar to those of the penta-adducts obtained by the organocopper routes.<sup>2,7</sup> Note that these new complexes cannot be synthesized by our previous organocopper route (allyl and benzyl copper reagents as well as an ester- or imide-containing Grignard reagents are unstable or unavailable).

The sequential hydrometalation/deprotonation/alkylation method has several noteworthy features. The hydroferration takes place regioselectively to introduce hydrogen atoms specifically around the ferrocene moiety. These protons in the “benzylic positions” can be removed very easily with hydroxide anion to generate a highly delocalized anion, which has a finite lifetime at room temperature. This anion reacts quickly with an alkyl halide exclusively at the carbon atoms where the protons were attached in the hydrofullerene starting materials. The properties of the anionic intermediates involved in the present synthetic sequence are an intriguing subject of future studies.

Even with the limited number of examples, we expect that the new synthetic methodology will significantly expand the variety of  $\eta^5$ -metal–fullerene complexes and hence will expand the utilities of such complexes in chemistry, biology, and materials science.<sup>9,10</sup> For instance, one can readily see the possibility of attaching the metal–fullerene complexes to a preexisting molecular structure through manipulation of the side chains,<sup>11</sup> and the removal of the Cp ring<sup>12</sup> for further conversion<sup>9f</sup> of the metal complex.

**Acknowledgment.** We thank Mobukagakusho, Japan, for financial support (Grant-in-Aid for Scientific Research, Specially Promoted Research and the 21st Century COE Program for Frontiers in Fundamental Chemistry), and M.T. thanks the Japan Society for Promotion of Science for predoctoral fellowship.

**Supporting Information Available:** Synthetic procedures of the new compounds and  $^1\text{H NMR}$  spectra of **6** and its deprotonated product (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Togni, A.; Hayashi, T. *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*; Wiley-VCH: Weinheim, 1995.
- (2) (a) Sawamura, M.; Iikura, H.; Nakamura, E. *J. Am. Chem. Soc.* **1996**, *118*, 12850. (b) Iikura, H.; Mori, S.; Sawamura, M.; Nakamura, E. *J. Org. Chem.* **1997**, *62*, 7912. (c) Sawamura, M.; Iikura, H.; Ohama, T.; Hackler, U. E.; Nakamura, E. *J. Organomet. Chem.* **2000**, *599*, 32. (d) Nakamura, E.; Sawamura, M. *Pure Appl. Chem.* **2001**, *73*, 355.
- (3) Toganoh, M.; Matsuo, Y.; Nakamura, E. *Angew. Chem., Int. Ed.* **2003**, *42*, 3530.
- (4) Subramanian, R.; Kadish, K. M.; Vijayashree, M. N.; Gao, X.; Jones, M. T.; Miller, M. D.; Krause, K. L.; Suenobu, T.; Fukuzumi, S. *J. Phys. Chem.* **1996**, *100*, 16327.
- (5) Sawamura, M.; Toganoh, M.; Suzuki, K.; Hirai, A.; Iikura, H.; Nakamura, E. *Org. Lett.* **2000**, *2*, 1919.
- (6) Upon heating in PhCN,  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2]_2$  generates ferrocene and cyclopentadiene, which was identified, during the synthesis of **1**, in the form of a Diels–Alder adduct with fullerene.
- (7) (a) Sawamura, M.; Kuninobu, Y.; Toganoh, M.; Matsuo, Y.; Yamanaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **2002**, *124*, 9354. (b) Nakamura, E. *Pure Appl. Chem.* **2003**, *75*, 427.
- (8) (a) Meier, M. S.; Bergosh, R. G.; Gallagher, M. E.; Spielmann, H. P.; Wang, Z. *J. Org. Chem.* **2002**, *67*, 5946. (b) Rubin, Y.; Ganapathi, P. S.; Franz, A.; An, Y.-Z.; Qian, W.; Neier, R. *Chem. Eur. J.* **1999**, *5*, 3162.
- (9) (a) Sawamura, M.; Kuninobu, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2000**, *122*, 12407. (b) Sawamura, M.; Nagahama, N.; Toganoh, M.; Hackler, U. E.; Isobe, H.; Nakamura, E.; Zhou, S.; Chu, B. *Chem. Lett.* **2000**, 1098. (c) Zhou, S.; Burger, C.; Chu, B.; Sawamura, M.; Nagahama, N.; Toganoh, M.; Hackler, U. E.; Isobe, H.; Nakamura, E. *Science* **2001**, *291*, 1944. (d) Sawamura, M.; Kawai, K.; Matsuo, Y.; Kanie, K.; Kato, T.; Nakamura, E. *Nature* **2002**, *419*, 702. (e) Nakamura, E.; Tahara, K.; Matsuo, Y.; Sawamura, M. *J. Am. Chem. Soc.* **2003**, *125*, 2834. (f) Matsuo, Y.; Nakamura, E. *Organometallics* **2003**, *22*, 2554.
- (10) (a) Guldi, T. M. *Chem. Soc. Rev.* **2002**, *31*, 22. (b) Tagmatarchis, N.; Prato, M. *Synlett* **2003**, 768. (c) Nierengarten, J. F.; Armaroli, N.; Accorsi, G.; Rio, Y.; Eckert, J. F. *Chem. Eur. J.* **2003**, *9*, 37. (d) Nakamura, E.; Isobe, H. *Acc. Chem. Res.* **2003**, *36*, In press.
- (11) Isobe, H.; Mashima, H.; Yorimitsu, H.; Nakamura, E. *Org. Lett.* **2003**, *5*, In press.
- (12) Matsuo, Y.; Kuninobu, Y.; Ito, S.; Nakamura, E. *Chem. Lett.* **2003**, In press.

JA037335B