Synthesis and Electrochemistry of Double-Decker Buckyferrocenes

Yutaka Matsuo,[†] Kazukuni Tahara,[‡] 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

Received February 18, 2006; E-mail: nakamura@chem.s.u-tokyo.ac.jp

Synthesis and multistep redox properties of polymetallic complexes linked by a π-electron-conjugated system continue to attract the interest of inorganic chemists and of those interested in molecular-level electronics.[1,2] As the result of such interest, the electronic effects of conjugated linkers, such as polyene,[3] polyphenylenes,[4] polyynes,[5] cumulene,[6] and polyaromatics,[7] on the electronic properties of dimetallic complexes have already been examined. This communication reports on the synthesis and electrochemistry of a new class of linked diferrocenes that we call double-decker buckyferrocenes **4** and **5** (Figure 1). The linker unit consists of a hoop-shaped, 40π-electron [10]cyclophenacene[8] and homoconjugatively allows electronic communication between the two ferrocene moieties.

We synthesized the target compounds through two different routes. In the first route, we started with the previously reported cyclophenacene compounds **1** and **2**.[8,9] Treatment of **1** with 5 equiv of [FeCp(CO)$_2$]$_2$ in PhCN at 185 °C afforded in a single step a C_{5v}-symmetric pentamethyl–pentaphenyl double-decker buckyferrocene, Fe$_2$(C$_{60}$Me$_5$Ph$_5$)Cp$_2$ (**4**), in 26% isolated yield (Scheme 1). We then surmised that the metalation reaction may also be applicable to the cyanofullerene **2**, which is a synthetic precursor to **1**.[8] Thus, **2** was treated similarly with [FeCp(CO)$_2$]$_2$ to obtain **4** in a better isolated yield of 47%. We consider that electron transfer from the Fe(I) complex to the cyclophenacene system occurred first and was followed by intramolecular electron transfer to the cyclopentadienyl moieties,[10] leading to the loss of hydride and cyanide anions, and eventually produced the desired Fe(II) complex **4**.

We relied on a second route to achieve the synthesis of the D_{5d} decamethyl compound **5** since the method to synthesize the pentamethyl–pentaphenyl compounds afforded an inseparable mixture of products. Thus, the pentamethyl buckyferrocene **3**[11] was first pentamethylated with a methylcopper reagent[12] and then metalated by [FeCp(CO)$_2$]$_2$ in PhCN to obtain Fe$_2$(C$_{60}$Me$_{10}$)Cp$_2$ (**5**) in 3% isolated yield after HPLC separation.[13]

The diiron complexes were characterized by ^{1}H and ^{13}C NMR, high-resolution APCI-TOF mass spectra, and X-ray single-crystal analyses (Figure 1; details given in Supporting Information). X-ray analyses of **4** and **5** showed that the bond alternation pattern characteristic of [10]cyclophenacene[8] was not disturbed by the metal complexation, whereas the fluorescence observed in **1** and **2** was not observed any more.[8]

The double-decker ferrocenes retain the basic electrochemical characteristics of ferrocene and [10]cyclophenacene and were found to reversibly undergo two successive one-electron oxidation and two successive one-electron reduction processes. The C_{5v} complex **4** in PhCN shows stepwise two-electron oxidation waves at 0.08 and 0.36 V (vs Fc/Fc$^+$) (data in Supporting Information). Such a large magnitude of the first and the second potentials is partly due

† Nakamura Functional Carbon Cluster Project, ERATO.
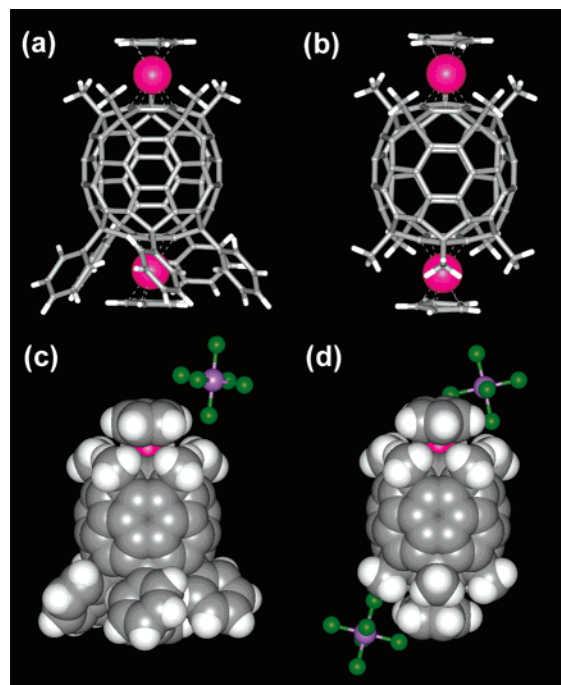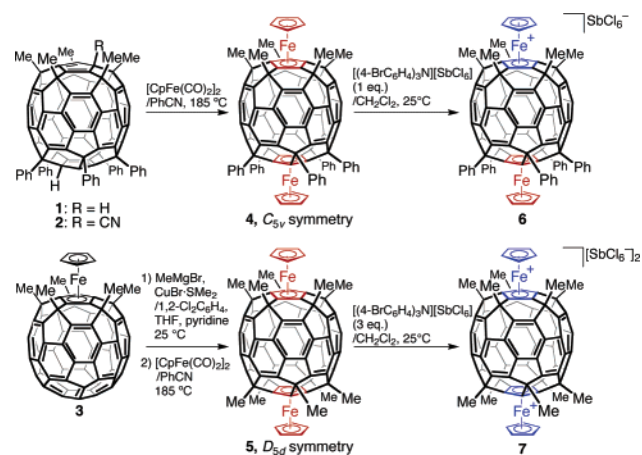‡ The University of Tokyo.

Figure 1. Molecular structures of diiron complexes determined by X-ray single-crystal analysis. (a) Stick drawing of **4**. (b) Stick drawing of **5**. (c) CPK drawing of **6**. (d) CPK drawing of **7**. Solvent molecules found in the unit cell are omitted for clarity. Details are given in Supporting Information.

Scheme 1

to electronic communication between the two ferrocene moieties (vide infra) and partly due to rather large electronic effects of the methyl and the phenyl groups that are connected to the fullerene core only through sp^3 carbon centers. By comparison with the oxidation potentials of the pentamethyl monoferrocene **3** and its pentaphenyl analogue,[11e] the first wave was assigned to the
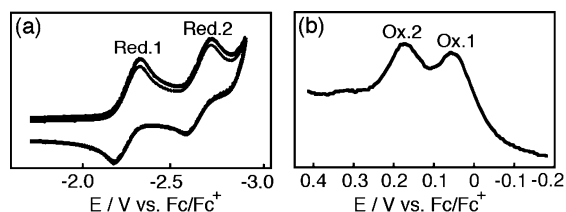
Figure 2. Electrochemistry of double-decker buckyferrocenes. (a) Cyclic voltammogram of reduction of **4**. Measurements were performed at the scan rate of 100 mV/s at 25 °C in THF containing [^{n}Bu$_4$N][ClO$_4$] as supporting electrolyte. (b) Differential pulse voltammogram of oxidation of **5**. Measurements were performed at 25 °C in PhCN containing [^{n}Bu$_4$N][ClO$_4$] as supporting electrolyte.

oxidation of the top iron atom surrounded by the electron-donating methyl groups and the second one to the bottom one. This assignment was confirmed by the crystal structure of a monocation [Fe$_2$(C$_{60}$Me$_5$Ph$_5$)Cp$_2$][SbCl$_6$] (**6**) (Figure 1c) that was obtained by chemical oxidation of **4** with 1 equiv of [(4-BrC$_6$H$_4$)$_3$N][SbCl$_6$] (Scheme 1). The geometry of the top ferrocene is similar to that of the parent ferrocenium cation,[14] while that of the bottom one is similar to the parent neutral compound.

The [10]cyclophenacene part accepts two electrons and forms 41π- and 42π-electron-conjugated systems, as indicated by the two reversible one-electron reduction waves at $E_{1/2}$ = −2.24 and −2.63 V (vs Fc/Fc$^+$ in THF) shown in Figure 2a. Chemical reduction of **5** with potassium metal under anaerobic conditions afforded an NMR-silent green-colored monoanion, and then a dark green-colored dianion as the amount of the reducing agent was increased. Absorptions at 750 and 1190 nm for the monoanion and 680 and 1000 nm for the dianion are characteristic of polyanions of substituted fullerenes (data in Supporting Information).[15] The mono- and dianions are thermally stable (for 2 days at 25 °C), but are rapidly oxidized by molecular oxygen giving back **5**.

The oxidation chemistry of the D_{5d}-symmetric compound **5** showed that the two iron atoms in **5** interact with each other through the hoop-shaped π-conjugation of the cyclophenacene linker. Differential pulse voltammetry (DPV) measurement of **5** exhibited a pair of overlapping but resolved oxidation waves (0.06 and 0.17 V vs Fc/Fc$^+$) (Figure 2b). The 110 mV separation of the two oxidation potentials (ΔE) is comparable to those of phenylene-linked diferrocenes (ΔE = 131, 90, and 104 mV for o-, m-, and p-C$_6$H$_4$),[4b,c] but larger than that of a biphenylene-linked diferrocene (ΔE = 70 mV).[4a]

The dication of **5** was synthesized and isolated as [Fe$_2$(C$_{60}$Me$_5$-Ph$_5$)Cp$_2$][SbCl$_6$]$_2$ (**7**) (Scheme 1). The X-ray crystal structure of **7** (Figure 1d) confirmed that the two ferrocene structures have been oxidized (Fe−C(Cp) = 2.10 Å and Fe−C(C$_{60}$) = 2.13 Å).

In conclusion, we have developed two synthetic approaches to the double-decker buckyferrocenes. These approaches are potentially suitable for synthesis of a variety of bimetallic [60]fullerene metal complexes possessing symmetric and dissymmetric organic substitution patterns and the same or different metal atoms. The multistep redox behavior accepting and giving up a total of at least four electrons makes these complexes interesting subjects of inorganic and materials studies. We recently showed that photo-excitation of the buckyferrocene **3** results in the formation of a charge-separated state (ferrocenium and fullerene radical anion),[16] and this result agrees with the presence of electronic communication between the two ferrocene moieties in **5**. Given the self-assembling

behavior of pentaorganofullerene derivatives,[17] higher-order aggregated structures of the dimetallic complexes will be an intriguing subject of further studies. Finally, we expect that the present synthetic method will also be useful for the synthesis of multimetallic derivatives of higher fullerenes and carbon nanotubes.[18]

Supporting Information Available: Procedures for synthesis of the new complexes, crystallographic data of **4**, **5**, **6**, and **7** (including CIF files), electrochemical data, and detail of theoretical study. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) As in synthesis of **1** (ref 8c), the major product of the methylcopper addition to **3** was the addition to a side pentagon rather than to the bottom pentagon (forming **5**) and was isolated with great difficulty.
(14) Bond lengths of Fe−C(Cp) (2.11 Å) and Fe−C(C$_{60}$) (2.13 Å) of the ferrocenium moiety surrounded by the methyl groups are longer than those (Fe−C(Cp) = 2.07 Å and Fe−C(C$_{60}$) = 2.08 Å) of the ferrocene moiety surrounded by the phenyl groups.
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