J|A|C|S
COMMUNICATIONS

Published on Web 07/18/2002

Hybrid of Ferrocene and Fullerene

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Received March 1, 2002

Ferrocene, reported half a century ago,[1] is composed of a pair of 6π-electron pentagonal carbon arrays and a 6d-electron iron(II) atom, while fullerene[2] is a 60 π-electron system including 12 pentagonal sp[2] carbon arrays. An idea of synthesizing "bucky ferrocene" through face-to-face fusion of the two molecules is intriguing, since such a molecule would enjoy the rich scientific heritage of both ferrocene and fullerene. However, the molecule so far remained hypothetical.[3] We report here that ferrocene/fullerene hybrid molecules **2** and **4** can be synthesized as singlet ground-state molecules by the use of suitably modified fullerene derivatives that can act as a 6π-electron donor ligand to the 6d-electron iron(II) atom.[4]

The hybrid molecule Fe($C_{60}Me_5$)Cp (**2**, abbreviated as Fe(FCp)-Cp) was first obtained in 10% yield by metathetical reaction[5] between FeBrCp$(CO)_2$ and a thallium complex of pentamethylated [60]fullerene Tl($C_{60}Me_5$).[6] We then discovered a more expeditious, C−H bond activation route that directly replaces the cyclopentadienyl hydrogen atom with the FeCp fragment of the Fe(I) complex. Heating $C_{60}Me_5H$ (**1**) and $[FeCp(CO)_2]_2$ together in benzonitrile at 180 °C for 8 h produced **2** in 52% isolated yield (Figure 1).[7] Both the syntheses of **1** and **2** being possible on a large scale, **2** was obtained in two steps from [60]fullerene in 45% overall yield on a multigram scale (see ref 7 and Supporting Information). The compound **2** was found to be extremely stable: no decomposition took place after **2** was left to stand for many months in air, after 24 h at 200 °C in vacuo, or after irradiation in benzene with a high-pressure mercury lamp under nitrogen for 15 h.

Recrystallization of **2** from CS_2/ethanol afforded single dark red crystals composed of a 1:1 mixture of **2** and CS_2 (Figure 2). The five methyl groups attached to five sp[3] carbon atoms protrude outward at an angle of 42° relative to the symmetry axis of the molecule, and the methyl and Cp hydrogen atoms are in van der Waals contact with each other. The Cp group and cyclopentadienide in FCp are arranged in a staggered manner. All C−C bond lengths in each pentagon are equal to each other within experimental error (1.411 ± 0.018 Å for Cp, and 1.425 ± 0.007 Å for the pentagon within FCp), and hence both cyclopentadienide rings are aromatic. The distances between the pentagon carbon atoms and the iron (2.033 Å for Cp−Fe, and 2.089 Å for FCp−Fe) are comparable to those in known ferrocene derivatives.[8] One reason for the longer FCp−Fe bond may be the nonplanarity of the bottom cyclopentadienide in FCp, which forces the 2p carbon orbitals away from the iron atom.

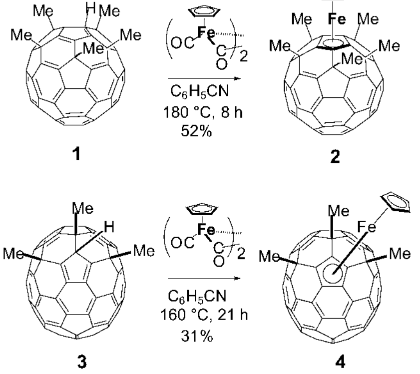

Figure 1. Synthesis of ferrocene/fullerene hybrid molecules **2** and **4**. The single and double bonds shown in [70]fullerene compounds are only formal as for [70]fullerene itself.

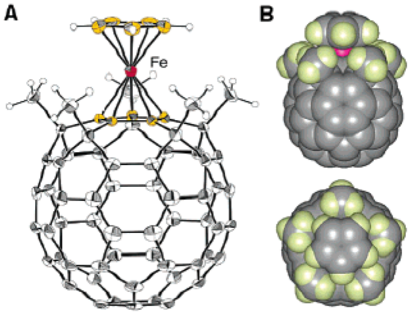

Figure 2. Molecular structure of ferrocene/[60]fullerene hybrid **2** determined by X-ray diffraction. (A) ORTEP drawing with 30% probability level ellipsoids. The CS_2 molecule found in the unit cell was omitted for clarity. (B) Space-filling models.

^1H and ^{13}C NMR spectra at −50 and 30 °C indicated that **2** has C_{5v} symmetry (only 10 ^{13}C NMR signals), and that the methyl groups rotate freely (a single signal at δ 2.51 ppm). The Cp protons resonate at δ 4.86 ppm, which indicates the aromaticity of the 6π-Cp group. The signal is notably shifted downfield compared with that for normal ferrocene (δ 4.16 ppm). The ^{13}C NMR signal of the Cp carbon atoms (δ 77.54 ppm) is also at a lower field than in ferrocene (δ 67.91 ppm), and the cyclopentadienide carbons in FCp resonate even more downfield (δ 91.86 ppm), indicating strong electron-withdrawing effects of the fullerene moiety. The UV/visible spectrum is similar to those of [60]fullerene and related organic derivatives. Like ferrocene, **2** gives no EPR signals. The hybrid compound can not only be oxidized reversibly like ferrocene but can also be reduced reversibly like fullerene (cyclic voltammetry measurement, CV). The one-electron oxidation potential of **2** ($E_{1/2}$) is +0.22 V relative to ferrocene; namely, **2** is more difficult to oxidize than ferrocene due to the electron-withdrawing effect of the fullerene moiety. The reduction potential of **2** is −1.46 V, which is comparable to that of the parent molecule $C_{60}Me_5H$ (−1.45 V). Note that ferrocene cannot be reduced under normal CV conditions. Such physicochemical properties of **2** are consistent with the

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10.1021/ja026069j CCC: $22.00

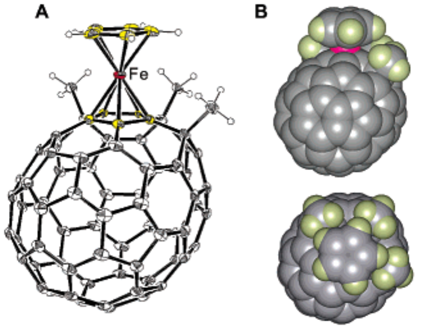

Figure 3. Molecular structure of ferrocene/[70]fullerene hybrid **4** determined by X-ray diffraction. (A) ORTEP drawing with 30% probability level ellipsoids. The CS_2 molecule found in the unit cell was omitted for clarity. (B) Space-filling models.

presence of conjugation between the bottom C_{50} moiety and the Cp anionic moiety using the 2p orbital lobes inside the fullerene core as previously reported.[6]

To synthesize a closer analogue of the parent "bucky ferrocene" where the one Cp moiety of ferrocene is directly conjugated with fullerene, we focused our attention on the trimethylated [70]fullerene $C_{70}Me_3H$ (**3**).[9] The metathesis approach failed entirely for the synthesis of **2**. Instead, we treated $C_{70}Me_3H$ (**3)** with $[FeCp(CO)_2]_2$ in benzonitrile at 160 °C for 21 h to obtain **4** in 31% isolated yield as a dark brown solid (Figure 1). An overall yield of the two-step synthesis from [70]fullerene was 27%. ^1H and ^{13}C NMR spectra at 25 °C indicated that **4** is C_s symmetric and that the methyl groups rotate freely (singlet signals at δ 2.81 (3H) and 2.93 ppm (6H)). The Cp protons resonate also as a singlet at δ 4.89 ppm, indicating free rotation of the Cp group. The ^{13}C NMR signal of the Cp carbon atoms resonate at a single frequency of δ 69.46 ppm, and the cyclopentadienide carbons in FCp at δ 88.03, 89.22, and 98.24 ppm.

Recrystallization of **4** from CS_2/pentane afforded single dark red crystals composed of a 1:1 mixture of **4** and CS_2. The X-ray crystal structure of **4** is shown in Figure 3. The structural features of the ferrocene moiety in **4** are similar to those of **2**. The distances between the pentagon carbon atoms and the iron (average 2.054 Å for Cp−Fe, and 2.083 Å for fullerene cyclopentadienide−Fe) as well as the C−C bond lengths in the Cp ligand, 1.41−1.43 Å, are comparable to those of ferrocene and **2**. A small but significant difference between **2** and **4** is that the cyclopentadienide C−C bond (1.458 Å, Figure 4A) connected to a hexagon in the "belt region" of [70]fullerene core is slightly longer than the remaining four C−C bonds in the pentagon, a feature known for indenyl iron complexes (Figure 4B).[10] Bond alternation found in the six-membered ring next to the cyclopentadienide moiety is another characteristic of an indenyl complex. Thus, the new compound **4** can be regarded as a "super-indenyl" iron(II) complex or alternatively as a member of new organometallic π (FCp,Cp)−d(Fe) systems incorporated into graphitic structure.

We have synthesized molecular hybrids of ferrocene and fullerene. Given the availability of a variety of synthetic method to modify the ferrocene moiety,[11] the versatile chemistry of the fullerene core,[5,6] and the self-organization of modified fullerenes,[12,13] we anticipate that these hybrid molecule will serve as key compounds in chemistry and material science. The new synthetic methodology proven for [60]- and [70]fullerene derivatives would be applicable to the construction of ferrocene structures on higher fullerenes and on the end cap region of carbon nanotubes and nanohorns.

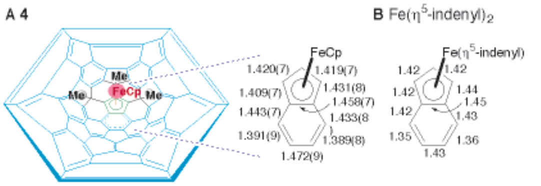

Figure 4. Indenyl iron(II) structure identified in **4** (A) compared with that of Fe(η^5-indenyl)$_2$ (B). Bond lengths are in angstroms deviation).

Supporting Information Available: Synthetic procedures, physical properties, and crystallographic data of the new compounds (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Synthesis of Fe(η^5-$C_{60}Me_5$)(η^5-C_5H_5) (**2**): A mixture of $C_{60}Me_5H$ (**1**, 1.00 g, 1.25 mmol) and $[FeCp(CO)_2]_2$ (444 mg, 1.25 mmol) in benzonitrile (200 mL) was stirred at 180 °C for 8 h. After evaporation of solvent, the crude mixture was diluted with toluene, and the solution was passed through a pad of silica gel. Solvent was removed in vacuo, and the mixture was recrystallized from CS_2/ethanol to obtain Fe(η^5-$C_{60}Me_5$)(η^5-C_5H_5) (**2**) as air-stable orange microcrystals (592 mg, 52% yield). Spectral data are shown in the Supporting Information.

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JA026069J