The first methano-bridged diferrocenyl fullerene (C_{60})

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Abstract

The diferrocenylmethanobuckminsterfullerene **1** was synthesized and spectroscopically characterized. © 2000 Elsevier Science Ltd. All rights reserved.

Since Kroto et al.[1] prepared an intermolecular charge transfer complex of fullerene (C_{60}) with two ferrocene molecules, several attempts to synthesize covalently linked fullerene/ferrocene-based molecules[2–6] have been made to investigate intramolecular electron transfer phenomena between an electroactive ferrocene donor and fullerene acceptor. However, the number and type of these molecules are still limited to donor–bridge-acceptor type dyads such as mostly ferrocenyl fulleropyrrolidines.[2–6] In line with these aspects, we wish to report the first synthesis of the methano-bridged compound **1**, which contains two covalently bound ferrocene moieties.

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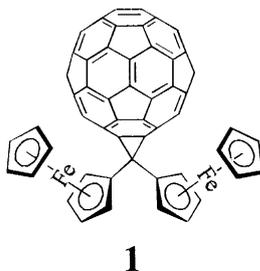
Starting from ferrocene **2**, diferrocenyl ketone **6** was synthesized by a slightly modified method of the literature procedure[7] (Scheme 1). The remaining steps for **7**, **8** and **1** were designed on the basis of the well-documented reactivity of C_{60} towards diazoalkanes already made accessible through a simple and reproducible route.[8–10] The cyclopropane bonds (ring closed 'methano-fullerene') thus obtained, connecting the C_{60} and the two ferrocenes are expected to exhibit a high π-character as already known structures.[11–13] This would allow conjugate interaction between the ferrocene and fullerene moieties.

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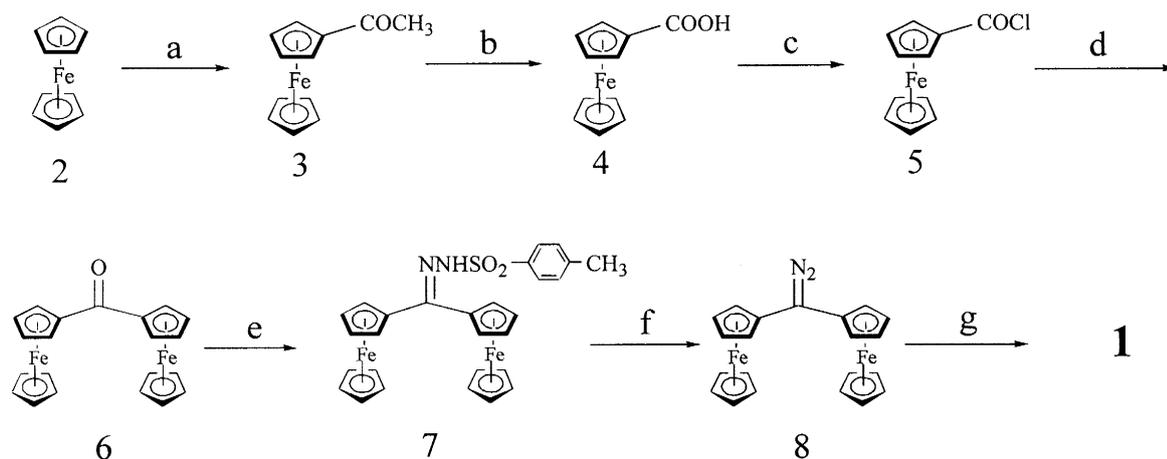
Scheme 1. (a) aceticanhydride, H_3PO_4, Δ; (b) NaOH, KI, I_2, H_2O, 12 h, rt, 12 h, reflux; (c) oxalyl chloride, 12 h, rt; (d) **2**, $AlCl_3$, CH_2Cl_2, 12 h, reflux; (e) p-toluenesulfonhydrazide, p-toluenesulfonic acid, 2 d, reflux; (f) EtONa, EtOH, 10 min, reflux; (g) C_{60}, toluene, 3 d, rt, 2 d, reflux

Acylation of commercially available ferrocene **2** gave **3** in 60% yield. Oxidation of **3** proceeded with NaOH and I_2 in water to afford **4** in 60% yield. Treatment of **4** with oxalyl chloride at room temperature provided acid chloride **5** and subsequent acylation with **2** gave the diferrocenyl ketone **6**[14] in 57% overall yield. Conversion of **6** with p-toluenesulfonhydrazide went smoothly to afford orange crystalline tosylhydrazone **7**[14] in a yield of 54%. Treatment of **7** with NaOEt produced the diazo derivative **8**, which is unstable under air and often changes back to **6** by reacting with oxygen during evaporation of the solvent. Therefore, without further separation and identification of **8**, we allowed the crude product **8** to react with C_{60} in toluene at room temperature for 3 days and then refluxed for 2 days. This led to the thermodynamically favored product **1** in 7.2% yield,[14] which has the structure of a closed 6,6-bridged methanofullerene with C_{2v} symmetry: FAB-mass spectrum of **1** showed peaks at m/z=1103 (M^+) and 720 (C_{60}). This provided direct evidence for the addition of the ferrocene moieties to the fullerene. ^1H NMR spectrum of **1** showed the typical resonance signals of the ferrocene ring protons at δ=4.13 (10H), 4.38 (4H) and 4.80 (4H) ppm. However, these ferrocene protons were shifted slightly to the upfield in comparison to **6**.

The ^{13}C NMR signals of ferrocene carbons in **1** were not markedly affected by substitution of C_{60}, but similarly shifted upfield compared to **6**. Four typical ferrocene carbon peaks of **1** appeared at δ=80.07, 72.74, 70.42 and 66.41 ppm. The complex pattern of 16 signals between 139.40 and 148.90 ppm was assigned to the C_{60} and also the resonance peak of the bridgehead carbon in **1** appeared at 94.29 ppm which lies near the usual region (70–90 ppm) of bridgehead carbons for methanofullerenes.[15,16] These patterns of signals are unambiguously diagnostic for the structure with a 6,6-junction. In addition, the signal for the quaternary methano–carbon in **1** appeared at 30.11 ppm as a distinct peak. This assignment is in good agreement with the previously reported assignments[17,18] (Fig. 1).

The UV/vis spectrum of **1** had some significant differences in comparison with **6**, but resembled those of other methanofullerene derivatives,[16,19] showing the characteristic absorption bands for the methanofullerenes at 430, 496, 579 and 698 nm, which newly appeared due to the incorporation of C_{60} into **6**. The electrochemical behavior of **1** showed two reduction waves at −0.6534 and −1.0229 V which are cathodically shifted compared to the first two reduction waves of C_{60} [−0.5993, −0.9688, −1.4099 V] measured by the same experimental conditions.[20] The incorporation of two ferrocene units was responsible for an additional shift to more negative values of the reduction potentials, thus indicating
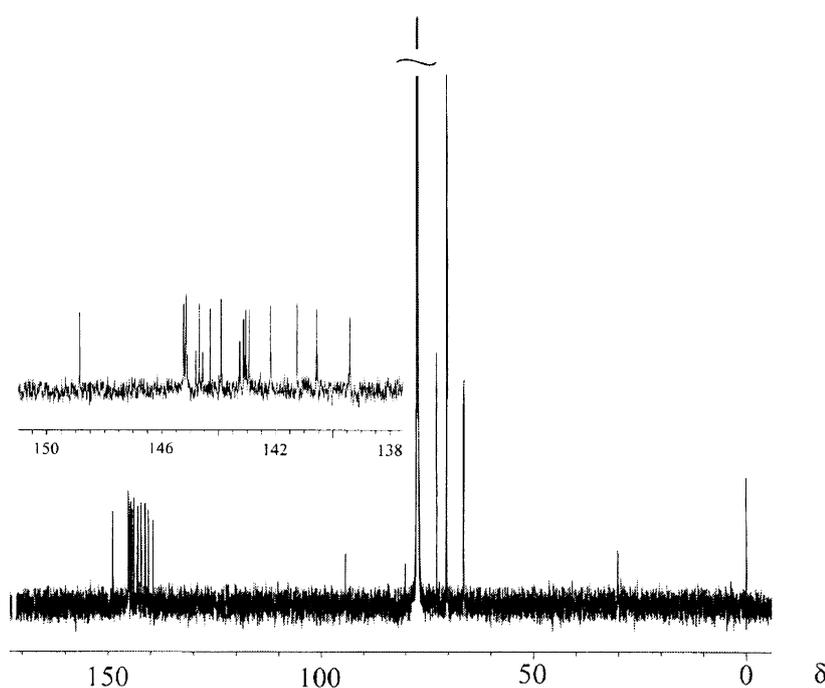
Fig. 1. ^{13}C NMR spectrum of **1** in CDCl$_3$:CS$_2$ (1:3). The inset shows an expansion of the aromatic region of the fullerene signals

the weak electronic interaction through the partially conjugate methanobridge between the ferrocene donor and the acceptor C$_{60}$ moiety. Further studies of this novel redox system using various conditions as well as the X-ray structural study of the compound **1** are currently under investigation, and we are also working on the synthesis of other metallocene analogues.

Acknowledgements

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14. Selected physical data for **6**, **7** and **1**. Compound **6**: m.p. >211°C (dec.). FT-IR: ν=3130, 3192, 1609, 1459, 1297 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ=5.00 (d, 4H), 4.52 (d, 4H), 4.20 (s, 10H). ^{13}C NMR (CDCl$_3$): δ=80.38, 71.40, 70.58, 69.94, 199.00 (C=O). UV/vis (CHCl$_3$): λ_{max} [nm]=241 (log ε=4.50), 273 (4.40), 359 (3.63), 480 (3.40) at 5.00×10^6 M. Satisfactory C and H analysis for C$_{21}$H$_{18}$Fe$_2$. Compound **7**: m.p. >180°C (dec.). FT-IR: ν=3097, 2952, 2850, 1346, 1163 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ=10.16 (s, 1H), 8.03 (d, 2H), 7.43 (d, 2H), 4.74 (d, 2H), 4.61 (d, 2H), 4.52 (d, 2H), 4.30 (d, 2H), 4.21 (d, 5H), 4.01 (s, 5H), 2.46 (s, 3H). Satisfactory C, H, N and S analysis for C$_{28}$H$_{26}$N$_2$O$_2$SFe$_2$. Compound **1**: m.p. >202°C (dec.). FT-IR: ν=2924, 2848, 1639, 1409 cm^{-1}. ^{1}H NMR (CDCl$_3$:CS$_2$=1:3): δ=4.8 (d, 4H), 4.38 (d, 4H), 4.13 (s, 10H). ^{13}C NMR (CDCl$_3$:CS$_2$=1:3): δ=148.85, 145.22, 145.14, 145.12, 144.80, 144.67, 144.29, 143.91, 143.25, 143.11, 143.05, 142.93, 142.17, 141.24, 140.57, 139.40, 94.29 (17 peaks), 80.07, 72.74, 70.42, 66.41, 30.11. UV/vis (orthodichlorobenzene): λ_{max} [nm]=258 (5.51), 270 (5.45), 329 (5.12), 363 (4.76), 430 (4.28), 496 (4.22), 579 (4.17), 698 (4.12) at 3.00×10^{-7} M. FAB-MS: *m/z* 1103 (M$^+$), 720 (C$_{60}$), 439, 391, 338, 286 (base peak) 133. Satisfactory C and H analysis for C$_{81}$H$_{18}$Fe$_2$.

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20. Cyclic voltametry data $E_{red.}/E_{ox.}$ for **1**: (3.00×10^{-4} M in *o*-dichlorobenzene with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, Pt working electrode, Ag/Ag$^+$ reference electrode, scan rate 50 mV/sec, 25°C) −0.6534/−0.5547, −1.0229/−0.9506 in volts; for [C$_{60}$] fullerene (5.05×10^{-4} M, Fc/Fc$^+$ as an internal standard), −0.5993/−0.4824, −0.9688/−0.8607, −1.4099/−1.2836 in volts.