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1,12-Diferrocenyldodecane at 100 K

1,12-Diferrocenyldodecane, [Fe$_2$(C$_5$H$_5$)$_2$(C$_{22}$H$_{32}$)], was synthesized from ferrocene and 1,12-dodecanediol chloride, followed by Clemmensen reduction. The single-crystal structure was determined at 100 K by X-ray diffraction and the spectroscopic and cyclic voltammetric data of 1,12-diferrocenyldodecane and its precursor are reported.

Comment

Ferroene-containing compounds have been extensively studied due to their unique structural and electrochemical properties. Ferrocenes have also been investigated with regard to their potential applications in chemical sensing, redox catalysts, ferromagnetism and self-assembled monolayers (Togni & Hayashi, 1995; Sawamura & Ito, 1992; Nicolosi et al., 1994; Sammakia et al., 1995; Beer et al., 1993; Zhang et al., 1995; Chidsey et al., 1990; Creager & Rowe, 1997) As an intermediate in the synthesis of self-assembled monolayers with multiple redox centers, 1,12-diferrocenyldodecane, (1), was synthesized via Clemmensen reduction of its precursor 1,12-diferrocenyldodecane-1,12-dione, (2), and its solid-state structure was established by X-ray diffraction at 100 K.

1,12-Diferrocenyldodecane crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the unit cell (Fig. 1). The center of each molecule is located on a crystallographic inversion center halfway between C16 and C16$^i$ [symmetry code: (i) $-x+1$, $-y+1$, $-z+2$]. The dodecane chain forms an extended zigzag chain. All torsion angles in the chain are close to 180$^\circ$ [between 175.70 (6)$^\circ$ for C12-C1-C1-C14 and 179.39 (6)$^\circ$ for C14-C1-C16-C15$^i$].

The C–C single bonds of the dodecane chain close to the ferrocene unit alternate slightly; the C10—C11 bond length between the ferrocene unit and the first methylene C atom is 1.501 (1) Å and that of C11—C12 is 1.529 (1) Å. All other C–C bond distances within the dodecane chain are identical within experimental error: 1.525 (1), 1.525 (1), 1.526 (1), 1.523 (1) and 1.525 (2) Å for C12—C13, C13—C14, C14—C15, C15—C16, and C16—C16$^i$, respectively. The bond distances within the ferrocene units are unexceptional, with the unsubstituted ring having basically identical C–C bond distances of 1.424 (2) Å, and C–C distances of the substituted
The Fe1···Fe1' distance within one molecule is 18.7196 (9) Å in the solid state. The closest Fe···Fe distances between different molecules are 6.3972 (3) Å for Fe1···Fe1'' [symmetry code: (ii) x, 4−y, z+1/2] and 7.1275 (3) Å for Fe1···Fe1iii [symmetry code: (iii) x, 1−y, z+1/2].

The solvent was removed in vacuo. The crude product was purified via column chromatography on silica with 75/25% hexanes/ethyl acetate as the eluent. The first band to elute (RF = 0.9) contained the desired product, viz. 1,12-diferrocenyldodecane, (1). 1H NMR (400 MHz, CDCl3): δ 1.199 [m, 16H, (CH3)2], 1.417 (m, 4H, CpCH2CH2), 2.228 (t, 4H, CpCH2), 3.976 (s, 4H, C6H4), 3.996 (s, 4H, C6H4), 4.032 (s, 10H, C6H4). MS: calculated for (2+), 538 m/z; found 538 m/z. CV [1.6 mm diameter Pt disc working, Pt wire counter, non-aqueous Ag/Ag+ reference electrodes, 1.0 m

Experimental

1,12-Diferrocenyldodecane-1,12-dione, (2), was synthesized from ferrocene and 1,12-dodecancenidyl chloride via the method of Chidsey et al. (1990) and was reduced to the title compound, (1), by Clemmensen reduction, as described by Creager & Rowe (1997). Ferrocene (35.00 g, 0.188 mmol) was dissolved in CH2Cl2 (250 ml). 1,12-Dodecancenidyl chloride (25.00 g, 0.0935 mmol) was added and the resulting solution was stirred for 5 min. Anhydrous AlCl3 (27.50 g, 0.207 mmol) was added and the solution was allowed to warm to room temperature and stirred for 1.5 h. De-ionized water (500 ml) was added dropwise and the mixture was stirred for an additional 1.5 h. The organic phase was washed with five portions of de-ionized water, then three times with brine, and dried over anhydrous sodium sulfate. The solvent was removed in vacuo. The crude product was purified via column chromatography on silica with 80/20% hexanes/ethyl acetate as the eluent. The second band to elute (RF = 0.75) contained the desired product, (2), in 12.2% yield. 1H NMR (400 MHz, CDCl3): δ 1.322 [m, 12H, (CH3)2], 1.701 (m, 4H, COCH2CH2), 2.692 (t, 4H, COCH2), 4.194 (s, 10H, C6H4), 4.487 (t, 4H, C6H4), 4.780 (t, 4H, C6H4). MS: calculated for (1+), 566 m/z; found 566 m/z. CV [1.6 mm diameter Pt disc working, Pt wire counter, non-aqueous Ag/Ag+ reference electrodes, 1.0 m

Crystal data

[Fe2(C6H5)2(C12H22)]

M_r = 538.36

Monoclinic, P2_1/c

a = 16.0203 (9) Å

b = 7.5367 (4) Å

c = 11.1773 (6) Å

β = 103.597 (1)°

V = 1311.73 (12) Å

Z = 2

Data collection

Bruker SMART APEX CCD diffractometer

3988 independent reflections

3769 reflections with I > 2σ(I)

Refinement

Refinement on F^2

wR(F^2) = 0.075

S = 1.07

3988 reflections

154 parameters

H-atom parameters constrained

All H atoms were placed in calculated positions, with a C—H bond distance of 0.99 (methylene) or 1.00 Å (Cp), and were refined with isotropic displacement parameters 1.2 times U_eq of the parent C atom. The s.u. values of the cell parameters are taken from the software, recognizing that the values are unreasonably small (Herbst, 2000).

Data collection: SMART (Bruker, 2002); cell refinement: SAINT-Plus (Bruker, 2003); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.
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References