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1,12-Diferrocenyldodecane at 100 K

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1,12-Diferrocenyldodecane, $[Fe_2(C_5H_5)_2(C_{22}H_{32})]$, was synthesized from ferrocene and 1,12-dodecanedioyl 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.

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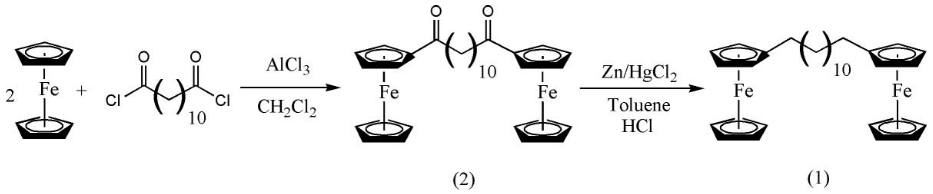
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.026
wR factor = 0.075
Data-to-parameter ratio = 25.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Ferrocene-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° [between 175.70 (6)° for C12$\cdots$C14$\cdots$C16 and 179.39 (6)° for C14$\cdots$C16$\cdots$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

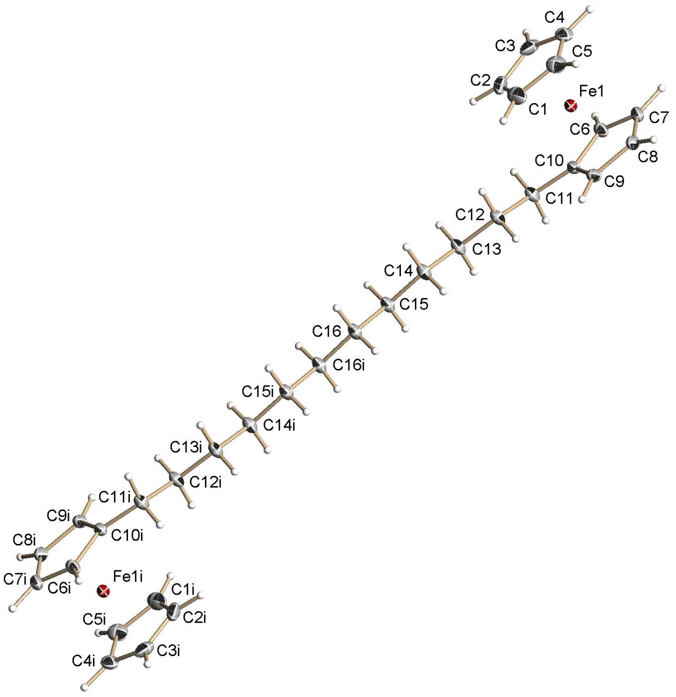


Figure 1

The molecular structure of (1), showing 50% probability displacement ellipsoids. [symmetry code: (i) $-x + 1$, $-y + 1$, $-z + 2$]

ring being between 1.429 (2) and 1.433 (2) Å.

The Fe1···Fe1^{i} 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^{ii} [symmetry code: (ii) x, $\frac{1}{2} - y$, $z + \frac{1}{2}$] and 7.1275 (3) Å for Fe1···Fe1^{iii} [symmetry code: (iii) x, $\frac{3}{2} - y$, $z + \frac{1}{2}$].

Experimental

1,12-Diferrocenyldodecane-1,12-dione, (2), was synthesized from ferrocene and 1,12-dodecanedioyl 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 at 273 K in CH_2Cl_2 (250 ml). 1,12-Dodecanedioyl chloride (25.00 g, 0.0935 mmol) was added and the resulting solution was stirred for 5 min. Anhydrous $AlCl_3$ (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 (300 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 (R_F = 0.75) contained the desired product, (2), in 12.2% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.322 [*m*, 12H, $(CH_2)_6$], 1.701 (*m*, 4H, $COCH_2CH_2$), 2.692 (*t*, 4H, $COCH_2$), 4.194 (*s*, 10H, C_5H_5), 4.487 (*t*, 4H, C_5H_4), 4.780 (*t*, 4H, C_5H_4). 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*M* (2), 0.1 *M* {(n–C_4H_9)N}ClO_4 in CH_3CN]: reversible single, two-electron oxidation centered at E° = +266 mV. 1,12-Diferrocenyldodecane-1,12-dione, (2) (9.02 g, 0.0158 mol), dissolved in toluene (800 ml), was mixed with freshly prepared zinc/mercury amalgam [mercuric chloride (1.06 g, 0.039 mol), zinc dust (15.79 g, 0.024 mol), de-ionized water (30 ml) and 12.1 *M* HCl (40 ml)] and was refluxed under static argon for 20 h. Two additional 30 ml portions of 12.1 *M* HCl were added with an addition funnel after 6 and 12 h under reflux. Upon cooling, the organic phase was washed three times with de-ionized water and three times with brine, and was dried over anhydrous sodium sulfate. 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 (R_F = 0.9) contained the desired product, *viz*. 1,12-diferrocenyldodecane, (1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.199 [*m*, 16H, $(CH_2)_8$], 1.417 (*m*, 4H, $CpCH_2CH_2$), 2.228 (*t*, 4H, $CpCH_2$), 3.976 (*s*, 4H, C_5H_4), 3.996 (*s*, 4H, C_5H_4), 4.032 (*s*, 10H, C_5H_5). 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*M* (1), 0.1 *M* {(n–C_4H_9)N}ClO_4 in CH_3CN]: reversible single, two-electron oxidation centered at E° = −25 mV. Single crystals of (1) were grown from a 75/25% hexanes/ethyl acetate solution by slow evaporation.

Crystal data

$[Fe_2(C_5H_5)_2(C_{22}H_{32})]$
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^3
Z = 2

D_x = 1.363 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6072 reflections
θ = 2.7–30.5°
μ = 1.12 mm^{-1}
T = 100 (2) K
Block, red
0.47 × 0.29 × 0.25 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS* in *SAINT-Plus*; Bruker, 2003)
T_{min} = 0.644, T_{max} = 0.75
15 135 measured reflections

3988 independent reflections
3769 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 30.5°
$h = -22 \rightarrow 22$
$k = -10 \rightarrow 10$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.075
S = 1.07
3988 reflections
154 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 0.3363P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

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 (Herbstein, 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

Beer, P. D., Crowe, D. B., Ogden, M. I., Drew, M. G. B. & Main, B. (1993). *J. Chem. Soc. Dalton Trans.* pp. 2107–2116.

Bruker (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2002). *SMART for WNT/2000*. Version 5.630. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2003). *SAINT-Plus*. Version 6.45. Bruker AXS Inc., Madison Wisconsin, USA.

Chidsey, C. E. D., Bertozzi, C. R., Putvinski, T. M. & Mujsce, A. M. (1990). *J. Am. Chem. Soc.* **112**, 4301–4306.

Creager, S. E. & Rowe, G. K. (1997). *J. Electroanal. Chem.* **420**, 291–299.

Herbstein, F. H. (2000). *Acta Cryst.* B**56**, 547–557.

Nicolosi, G., Patti, R., Morrone, R. & Piatelli, M. (1994). *Tetrahedron Asymmetry*, **5**, 1639–1642.

Sammakia, T., Latham, H. A. & Schaad, D. R. (1995). *J. Org. Chem.* **60**, 10–11.

Sawamura, M. & Ito, Y. (1992). *Chem. Rev.* **92**, 857–871.

Togni, A. & Hayashi, T. (1995). Editors. *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*. Weinheim, Germany: Verlag Chemie.

Zhang, L., Godinez, L. A., Lu, T., Gokel, G. W. & Kaifer, A. E. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 235–237.

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