Crystal structure of (E)-1,2-diferrocenyl-1,2-bis(furan-2-yl)ethene

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Crystal structure of \((E)-1,2\)-diferroacenyl-1,2-bis(furan-2-yl)ethene

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The title compound, \([\text{Fe}_2(\text{C}_5\text{H}_5)_2(\text{C}_{20}\text{H}_{14}\text{O}_2)]\), is the product of a new synthetic route towards tetraaryl/hetaryl-substituted ethenes that reduces the occurrence of side-products. In the crystal, the molecule is centrosymmetric and the cyclopentadienyl (Cp) rings are nearly coplanar and aligned slightly closer to a staggered conformation than to an eclipsed one. The ethene plane is tilted by 32.40 (18)/\(C_{14}\) with respect to that of the substituted Cp ring and by 63.19 (19)/\(C_{14}\) with respect to that of the furan ring. C—H···π interactions link the molecules into a three-dimensional supramolecular framework.

1. Chemical context

Tetrasubstituted ethenes bearing aryl, hetaryl or ferrocenyl groups are of current interest, as many of them find applications as novel materials for photooptics, electronics, crystal engineering and as new medications (Astruc, 2017). Ethene derivatives with a ferrocenyl unit on one or both C atoms of the alkene deserve special attention. Prominent representatives of the first type are ferrocifene \{1-[4-(2-dimethylaminoethoxy)phenyl]-1-phenyl-2-ferrocenylbut-1-ene\} and its di-OH analogue, which are known as potent, organometallic antitumor drugs (Jaouen et al., 2015; Resnier et al., 2017). On the other hand, dimethyl \((Z)-2,3\)-diferrocenylbut-2-enedioate displays interesting redox and solvatochromic properties (Solntsev et al., 2011). As typical procedures for the preparation of tetrasubstituted ethenes containing a ferrocenyl substituent, conversions of the corresponding ketones under the McMurry reaction conditions (Top et al., 1997) or reduction coupling using low-valent titanium agents are recommended (Dang et al., 1990). In both cases, the reported yields are satisfactory to good, but a serious disadvantage is the formation of side-products. Recently, we reported a new approach to tetraaryl/hetaryl-substituted ethenes via desilylation of 2-(trimethylsilyl)-4,4,5,5-tetraaryl/hetaryl-1,3-dithiolanes, obtained from diaryl/hetaryl thioketones by treatment with \((\text{trimethylsilyl})\text{diazomethane (TMS-CHN}_2\)) at low temperature (Młośnò et al., 2017). The mechanism of this unusual conversion was explained by the assumption that the \textit{in situ}-generated 1,3-dithiolane anion undergoes a spontaneous cycloelimination \((\text{3} + \text{2}-\text{cycloreversion})\) to give the dithioformate anion and the corresponding tetrasubstituted ethene derivative. The same method was applied for the preparation of some ferrocenyl/hetaryl-substituted ethenes (Młośnò et al., 2018).
Here we report the analogous synthesis and crystal structure of the known title compound, (E)-1, with m.p. 485–487 K. For the previously described synthesis of this product (Dang et al., 1990), a m.p. of 489–491 K and a yield of 17% were reported and the authors tentatively assigned the (E)-configuration to the obtained compound. In our case, single crystals of (E)-1 were grown from hexane/CH₂Cl₂ and used for an X-ray diffraction analysis, from which the previous tentatively postulated structure of the obtained isomer could be confirmed.

2. Structural commentary

The molecule of (E)-1 sits across a crystallographic centre of inversion and is shown in Fig. 1. Within the asymmetric unit, the Fe atom sits very well centred between the cyclopentadienyl (Cp) rings with all Fe—C distances in the range 2.0352 (17)–2.0712 (16) Å. The Cp C—C bond lengths [mean 1.435 (2) Å] involving the substituted C atom, C6, are very slightly elongated compared with the other C—C distances [mean 1.418 (3) Å]. Other bond lengths and angles are unremarkable. The two Cp rings are aligned slightly closer to a staggered conformation than to an eclipsed one, with the ring rotation from perfectly eclipsed being 20.6 (2)° (18° is the halfway point between eclipsed and staggered). The dihedral angle between the planes of the two Cp rings in the ferrocenyl entity is only 4.08 (11)° and ethene atom C1 is coplanar with the Cp ring to which it is bonded. However, the ferrocenyl entity is tilted with respect to the ethene plane, with a dihedral angle between the plane of the substituted Cp ring and that of the ethene plane of 32.40 (18)°. The dihedral angle between the substituted Cp ring and the adjacent furan ring is 53.46 (11)°, while that between the plane of the furan ring and the ethene plane is 63.19 (19)°. The planes of the two furan rings are necessarily parallel because of the centre of inversion.

3. Supramolecular features

There are no significant C—H···O or π—π interactions, but some weak C—H···π interactions are present (Table 1). C8—H of the substituted Cp ring has an edge-on intermolecular interaction with the unsubstituted Cp ring at x + 1/2, y + 1/2, z (i.e., x, y, z + 1). This interaction leads to double-stranded chains or ladders, in which the molecule acts as the ladder rungs; the chains run parallel to the [001]...
4. Database survey

The Cambridge Structural Database (CSD, Version 5.39 with February 2018 updates; Groom et al., 2016) contains one entry for a 1,1-diferrocenylethene [1,1-bis(1′,2′,3′,4′,5′-pentamethylferrocen-1′-yl)ethene, CSD refcode CIJQAN, Heigl et al., 1999] and 24 entries involving related 1,2-diferrocenylethenes, 10 of which are (E)-isomers. The archetypal structure is (E)-1,2-diferrocenylethene (REBDAD, Denill et al., 1996), in which the Cp rings of the ferrocenyl entities adopt an almost perfectly eclipsed arrangement. With the exception of 1-(1′-benzoylferrocenyl)-2-ferrocenylethene and 1-(1′-(4-methoxybenzoyl)ferrocenyl)-2-ferrocenylethene (OJUWUN and OJUXAU, Roemer et al., 2016), in which the ferrocenyl Cp rings lie close to a staggered arrangement, all of the other structures of molecules with the (E)-configuration display Cp arrangements that are much closer to eclipsed than observed for (E)-1 (ACUVAV, Mata & Peris, 2001; IBAXAM, DeHope et al., 2011; IVOSE, Skibar et al., 2004; JANJAJ, Dong et al., 1989; OJUXEY, Roemer et al., 2016; QICKIW, Chen et al., 2000; REBDAD; WIMYOH, Nagahora et al., 2007, Roemer & Lentz, 2008, Farrugia et al., 2009). The 1,1-diferrocenylethene structure also has eclipsed Cp rings. The two staggered (E)-configured examples have a bulky substituent on one of the distal Cp rings; those with a less bulky Cp substituent have the eclipsed arrangement. Interestingly, (E)-1 has no Cp substituents yet the Cp ring arrangement deviates significantly from eclipsed. The degree of eclipsing of the Cp conformations found among the molecules with the (Z)-configuration, two of which have a cyclopene ring as the ethene bridge (AMODIP, Klimova, Berestneva, Ramirez et al., 2003; EQOMIG, Klimova, Berestneva, Cinquantini et al., 2003), is more varied (AMODOV and AMODUB, Klimova, Berestneva, Ramirez et al., 2003; BADDAM, Beletskaya et al., 2001, Solntsev et al., 2011; JAIYIF and JAIYOL, García, Flores-Alamo, Flores & Klimova, 2017; KIGQUO, Klimova et al., 2013; LUFCEW, García et al., 2014; QASPEI, QATDAT and QATDEX, García, Flores-Alamo, Ortiz-Frade & Klimova, 2017; QICKOC, Chen et al., 2000; TUJDEI, Klimova et al., 2009).

5. Synthesis and crystallization

The title compound was prepared according to the reaction sequence presented in the scheme below. A solution of thiketone 2 (297 mg, 1 mmol; prepared according to Mloston et al., 2015) in THF (3 ml) was cooled to 198 K (acetone/dry ice). Then, TMS-CHN₂ was added portion-wise to the mixture until the green colour of the starting thioketone disappeared. The magnetically stirred reaction mixture was allowed to warm slowly to ca 268 to 273 K and at this temperature a commercially available solution of tetrabutylammonium fluoride (TBAF, 1 ml, 1 M) was added in small portions. Stirring was continued for 20 min, and after warming to room temperature, the solvent was evaporated under vacuum. The crude product was analyzed by ¹H NMR spectroscopy, which revealed the presence of two isomeric ethenes in a ratio of ca 10:1. After column chromatography (SiO₂, CH₂Cl₂/hexane 3:7), the major product was isolated, contaminated with a small admixture of the minor one, as an analytically pure material, crystals suitable for the X-ray diffraction measurement were separated without additional recrystallization.

![Image](https://example.com/image.png)

**Figure 3**
The ladder motif running parallel to [001] formed by the C3H··π interactions.

[600 MHz, CDCl₃, δ (ppm), J (Hz)]; 3.63–3.65 [m, 4CH(Fc)], 4.13–4.15 [m, 4CH(Fc)], 4.16 [s, 10CH(Fc)], 6.40 [d, 3J_HH = 3.0, 2CH(Fur)], 6.54 [dd, 4J_HH = 1.8, 3J_HH = 3.0, 2CH(Fur)], 7.58 [brs, 2CH(Fur)].

¹³C NMR [150 MHz, CDCl₃, 627]
Table 2
Experimental details

| Crystal data | Chemical formula | $M_r$ | [Fe$_2$(C$_{5}$H$_{5}$)$_{2}$(C$_{20}$H$_{14}$O$_{2}$)] | 528.19 |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| Temperature (K) | 160 |
| $a$, $b$, $c$ (Å) | 5.81066 (13), 22.7138 (5), 8.38031 (18) |
| $\beta$ (°) | 91.785 (2) |
| $V$ (Å$^3$) | 1105.40 (4) |
| $Z$ | 2 |
| Radiation type | Mo Kα |
| $\mu$ (mm$^{-1}$) | 1.34 |
| Crystal size (mm) | 0.20 × 0.16 × 0.08 |

Data collection

Diffractometer

Oxford Diffraction SuperNova, dual-diffraction diffractometer

Absorption correction

Multi-scan (CrysAlis PRO; Rigaku OD, 2015)

$T_{min}$, $T_{max}$ | 0.985, 1.000 |

No. of measured, independent and observed | [I > 2$\sigma$(I)] | 13881, 3021, 2612 |

$R_{int}$ | 0.026 |

(sin $\theta$/2$\lambda$)$_{max}$ (Å$^{-1}$) | 0.708 |

Refinement

$R(F^2 > 2\sigma(F^2))$, wR($F^2$), $S$ | 0.032, 0.077, 1.04 |

No. of reflections | 3021 |

No. of parameters | 154 |

H-atom treatment | H-atom parameters constrained |

$\Delta$,$\rho_{max}$, $\Delta$,$\rho_{min}$ (e Å$^{-3}$) | 0.49, −0.36 |

Computer programs: CrysAlis PRO (Rigaku OD, 2015), SHELXT2014 (Sheldrick, 2015a), SHELXL2014 (Sheldrick, 2015b), ORTEPII (Johnson, 1976), Mercury (Macrae et al., 2006), PLATON (Spek, 2015) and publICIF (Westrip, 2010).

δ (ppm): 68.5, 68.9 [2 signals for 8CH(Fc)], 69.6 [10CH(Fc)], 85.4 [2C(Fc)], 109.1, 111.1, 140.8 [3 signals for 6CH(Fur)], 129.1 (C=C), 153.3 [2C(Fur)], ESI–MS (mixture of isomers): 528 (100, [M$^+$]), 529 (50, [M + 1$^+$]). Element analysis calculated for C$_{20}$H$_{14}$Fe$_2$O$_2$ (528.20): C 68.22, H 4.58%; found: C 68.38, H 4.61%.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were placed in geometrically calculated positions and were constrained to ride on their parent atom with C–H = 0.95 Å and with $U_{iso}$(H) = 1.2$U_{eq}$(C).

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