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*Acta Cryst.* (2018). **E74**, 625–629



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

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Received 26 March 2018

Accepted 29 March 2018

Edited by J. Simpson, University of Otago, New Zealand

**Keywords:** crystal structure; ethenes; ferrocene.

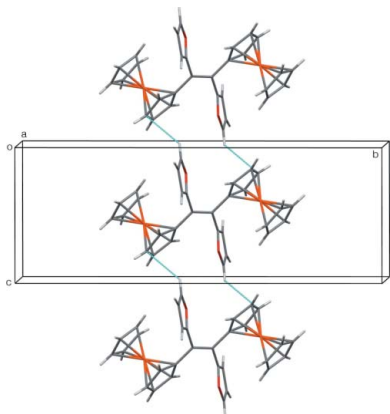
**CCDC reference:** 1833400

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The title compound, [Fe<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>20</sub>H<sub>14</sub>O<sub>2</sub>)], 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)<sup>o</sup> with respect to that of the substituted Cp ring and by 63.19 (19)<sup>o</sup> with respect to that of the furan ring. C—H ···π interactions link the molecules into a three-dimensional supramolecular framework.

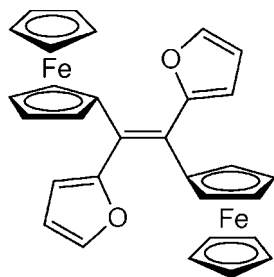
## 1. Chemical context

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 reductive 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 (trimethylsilyl)diazomethane (TMS-CHN<sub>2</sub>) at low temperature (Młostoń *et al.*, 2017). The mechanism of this unusual conversion was explained by the assumption that the *in situ*-generated 1,3-dithiolane anion undergoes a spontaneous cycloelimination ([3 + 2]-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 (Młostoń *et al.*, 2018).



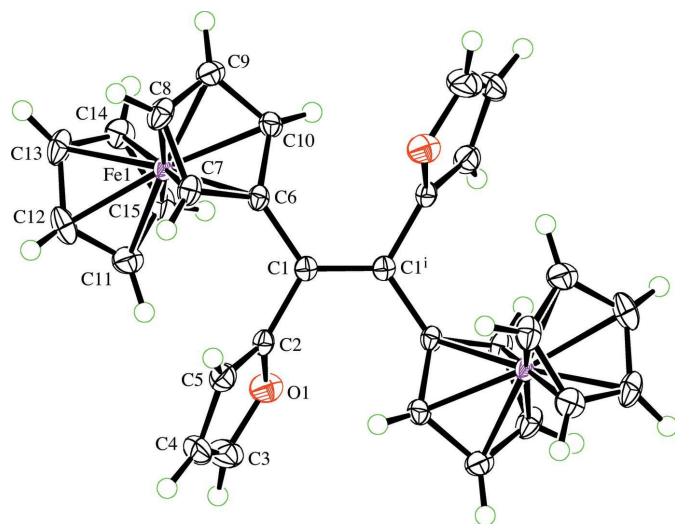
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Here we report the analogous synthesis and crystal structure of the known title compound, (*E*)-**1**, with m.p. 485–487 K. For the previously described synthesis of this product (Dang *et al.*, 1990), a m.p. of 489–491 K and a yield of 17% were reported and the authors tentatively assigned the (*E*)-configuration to the obtained compound. In our case, single crystals of (*E*)-**1** were grown from hexane/CH<sub>2</sub>Cl<sub>2</sub> 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 half-way point between eclipsed and staggered). The dihedral



**Figure 1**

The molecular structure of the title compound, (*E*)-**1**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .

**Table 1**

Hydrogen-bond geometry (Å, °).

Cg1, Cg2 and Cg3 are the centroids of the C6–C10, C11–C15 and C2/O1/C3–C5 rings, respectively.

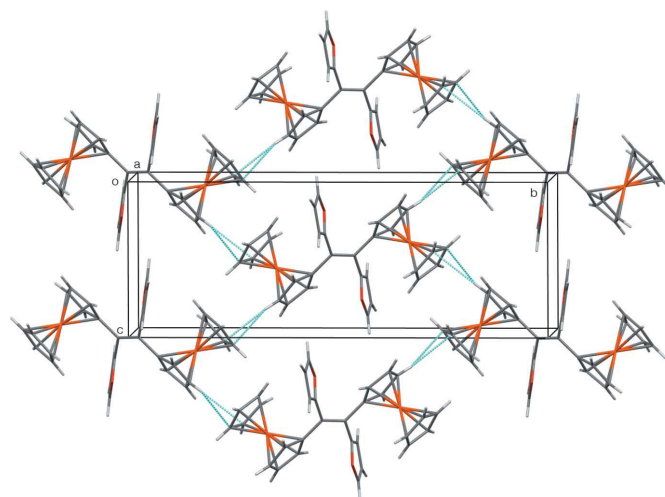
| <i>D</i> –H··· <i>A</i>      | <i>D</i> –H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> –H··· <i>A</i> |
|------------------------------|-------------|---------------|-----------------------|-------------------------|
| C3–H3···Cg1 <sup>i</sup>     | 0.95        | 2.81          | 3.686 (3)             | 153                     |
| C8–H8···Cg2 <sup>ii</sup>    | 0.95        | 2.85          | 3.764 (2)             | 161                     |
| C10–H10···Cg3 <sup>iii</sup> | 0.95        | 2.68          | 3.2097 (18)           | 116                     |

Symmetry codes: (i)  $x, y, z + 1$ ; (ii)  $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$ ; (iii)  $-x + 1, -y + 1, -z + 1$ .

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.

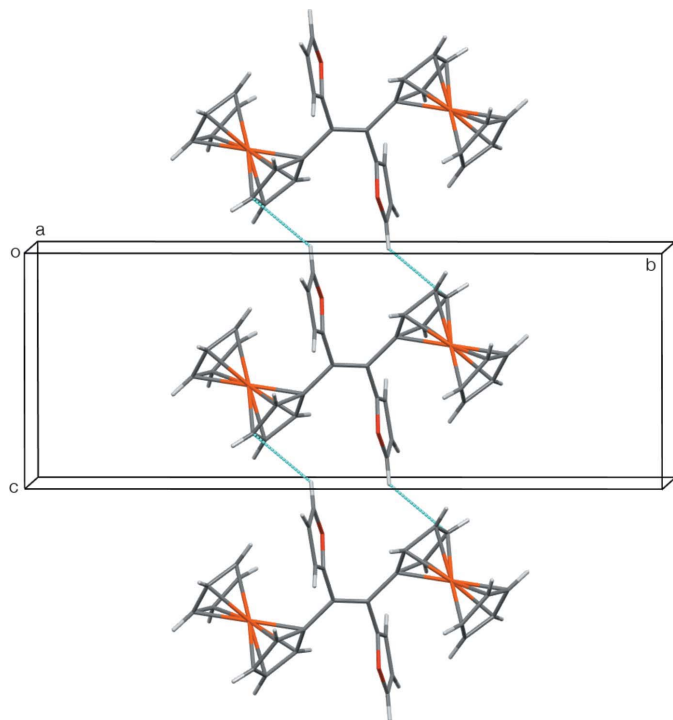
## 3. Supramolecular features

There are no significant C–H···O or  $\pi$ – $\pi$  interactions, but some weak C–H··· $\pi$  interactions are present (Table 1). C8–H of the substituted Cp ring has an edge-on intermolecular interaction with the unsubstituted Cp ring at  $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$ . The extension of this interaction through the molecular centre of inversion leads to sheets of molecules, which lie parallel to the (101) plane (Fig. 2). The furan ring, *via* C3–H, has an edge-on intermolecular C–H··· $\pi$  interaction with the substituted Cp ring at  $x, y, z + 1$ . 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]



**Figure 2**

The sheets of molecules lying parallel to the (101) plane formed by the C8–H··· $\pi$  interactions.



**Figure 3**  
The ladder motif running parallel to [001] formed by the C3—H... $\pi$  interactions.

direction (Fig. 3). Finally, C10—H of the substituted Cp ring interacts intramolecularly with the  $\pi$ -system of the furan ring at  $-x + 1, -y + 1, -z + 1$  on the opposite side of the molecule. This latter interaction is quite short, but has a sharp angle at the H atom (Table 1), so the arrangement might just be a consequence of the molecular conformation. The molecular inversion symmetry, in combination with the two types of intermolecular interactions, links the molecules into a three-dimensional supramolecular framework.

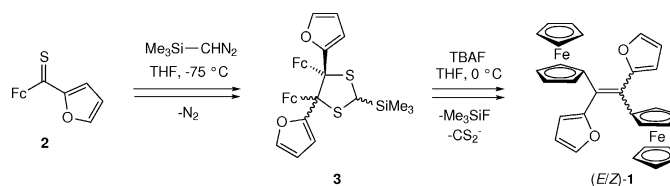
#### 4. Database survey

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''-penta-methylferrocen-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, Denifl *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; IVOSER, 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 cyclopropene 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; JAJYIF and JAJYOL, 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 thioketone **2** (297 mg, 1 mmol; prepared according to Mlostoń *et al.*, 2015) in THF (3 ml) was cooled to 198 K (acetone/dry ice). Then, TMS-CHN<sub>2</sub> 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 <sup>1</sup>H NMR spectroscopy, which revealed the presence of two isomeric ethenes in a ratio of *ca* 10:1. After column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/hexane 3:7), the major product was isolated, contaminated with a small admixture of the minor one, as an analytically pure sample (78% yield). After additional crystallization from a hexane/CH<sub>2</sub>Cl<sub>2</sub> mixture, 285 mg (54%) of pure (*E*)-**1** were isolated as orange crystals with m.p. 485–487 K. From this material, crystals suitable for the X-ray diffraction measurements were separated without additional recrystallization.



<sup>1</sup>H NMR [600 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm), *J* (Hz)]: 3.63–3.65 [*m*, 4CH(Fe)], 4.13–4.15 [*m*, 4CH(Fe)], 4.16 [*s*, 10CH(Fe)], 6.40 [*d*, <sup>3</sup>*J*<sub>H,H</sub> = 3.0, 2CH(Fur)], 6.54 [*dd*, <sup>4</sup>*J*<sub>H,H</sub> = 1.8, <sup>3</sup>*J*<sub>H,H</sub> = 3.0, 2CH(Fur)], 7.58 [*brs*, 2CH(Fur)]. <sup>13</sup>C NMR [150 MHz, CDCl<sub>3</sub>,

**Table 2**  
 Experimental details.

|  |   |
|--|---|
| Crystal data   |   |
| Chemical formula   | [Fe <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>20</sub> H <sub>14</sub> O <sub>2</sub> )] |
| <i>M</i> <sub>r</sub>  | 528.19  |
| Crystal system, space group  | Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>  |
| Temperature (K)  | 160   |
| <i>a</i> , <i>b</i> , <i>c</i> (Å)   | 5.81006 (13), 22.7138 (5),<br>8.38031 (18)  |
| $\beta$ (°)  | 91.785 (2)  |
| <i>V</i> (Å <sup>3</sup> )   | 1105.40 (4)   |
| <i>Z</i>   | 2   |
| Radiation type   | Mo <i>K</i> α   |
| $\mu$ (mm <sup>-1</sup> )  | 1.34  |
| Crystal size (mm)  | 0.20 × 0.16 × 0.08  |
| Data collection  |   |
| Diffraction  | Oxford Diffraction SuperNova,<br>dual-radiation diffractometer  |
| Absorption correction  | Multi-scan ( <i>CrysAlis PRO</i> ;<br>Rigaku OD, 2015)  |
| <i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>  | 0.895, 1.000  |
| No. of measured, independent and<br>observed [ <i>I</i> > 2σ( <i>I</i> )] reflections                          | 13881, 3021, 2612   |
| <i>R</i> <sub>int</sub>  | 0.026   |
| (sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )  | 0.708   |
| Refinement   |   |
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i> | 0.032, 0.077, 1.04  |
| No. of reflections   | 3021  |
| No. of parameters  | 154   |
| H-atom treatment   | H-atom parameters constrained   |
| Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )   | 0.49, -0.36   |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *ORTEP11* (Johnson, 1976), *Mercury* (Macrae *et al.*, 2006), *PLATON* (Spek, 2015) and *publCIF* (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]<sup>+</sup>), 529 (50, [M + 1]<sup>+</sup>). Elemental analysis calculated for C<sub>30</sub>H<sub>24</sub>Fe<sub>2</sub>O<sub>2</sub> (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*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C).

## Acknowledgements

GM thanks Professor Wolfgang Weigand (Jena) for stimulating discussions on the chemistry of ferrocene thioketones.

## Funding information

Funding for this research was provided by: Maestro-3 (grant No. Dec-2012/06/A/ST5/00219 to R. Hamera-Fałdyga, G. Mlostoń); Institutspartnerschaft, Alexander von Humboldt Foundation, Bonn (grant to R. Hamera-Fałdyga, G. Mlostoń).

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