# [3]Ferrocenophan-1-one

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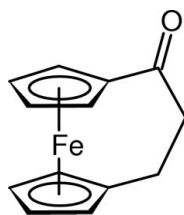Correspondence e-mail: stepnic@natur.cuni.cz

The crystal structure of [3]ferrocenophan-1-one, [Fe(C$_{13}$H$_{12}$O)], has been redetermined at 150 K. The tethered cyclopentadienyl (Cp) rings are tilted by 9.39 (18)° and assume an eclipsed conformation. The 1-oxopropane-1,3-diyl bridge has a pseudo-envelope conformation with the C=O group deviating by as much as 22.5 (2)° from coplanarity with its attached Cp ring.

## Related literature

For an overview of the chemistry of ferrocene, see: Štěpnička (2008). For the preparation of the title compound, see: Turbitt & Watts (1972). For its crystal structure at room temperature, see: Jones *et al.* (1965). For an introductory review on the chemistry of ferrocenophanes with carbon bridges, see: Heo & Lee (1999).



## Experimental

### Crystal data

| | |
|---|---|
| [Fe(C$_{13}$H$_{12}$O)] | $V$ = 966.07 (4) Å$^3$ |
| $M_r$ = 240.08 | $Z$ = 4 |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation |
| $a$ = 5.77450 (10) Å | $\mu$ = 1.52 mm$^{-1}$ |
| $b$ = 7.3303 (2) Å | $T$ = 150 (2) K |
| $c$ = 22.8596 (6) Å | $0.38 \times 0.30 \times 0.28$ mm |
| $\beta$ = 93.242 (2)° | |

### Data collection

| | |
|---|---|
| Nonius KappaCCD diffractometer | 13397 measured reflections |
| Absorption correction: multi-scan (*SORTAV*; Blessing, 1995) | 2223 independent reflections |
| | 2102 reflections with $I > 2\sigma(I)$ |
| $T_{min}$ = 0.579, $T_{max}$ = 0.660 | $R_{int}$ = 0.032 |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.038 | 136 parameters |
| $wR(F^2)$ = 0.096 | H-atom parameters constrained |
| $S$ = 1.31 | $\Delta\rho_{max}$ = 0.53 e Å$^{-3}$ |
| 2223 reflections | $\Delta\rho_{min}$ = −0.38 e Å$^{-3}$ |

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON* and *publCIF* (Westrip, 2008).

## References

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**supplementary materials**

## [3]Ferrocenophan-1-one

### P. Stepnicka and I. Císarová

### Comment

The chemistry of ferrocene has received considerable attention because of its widespread applications ranging from material science to biomedicine. A particularly successful area is undoubtedly catalysis with ferrocene ligands (Štěpnička, 2008). A number of ferrocene ligands has been prepared a studied as ligands for transtion metal-mediated reactions. Among the numerous ligands reported to date, a specific class is constituted by the donors whose cyclopentadienyl (Cp) rings are interconnected with a linking group (*i.e.*, ferrocenophane-type compounds (Heo & Lee, 1999)). [3]ferrocenophan-1-one (I) represent a convenient entry to such donors (Štěpnička, 2008). Because the crystal structure of I has been reported already in the middle 1960's (Jones *et al.*, 1965), we have redetermined it at 150 K in order to obtain more precise structural information.

The molecular structure of I (Figure 1) is rather unexceptional as far as interatomic distances and angles concerns. Because of spatial constraints imposed by the 1-oxapropan-1,3-diyl linker, the Cp rings are tilted by 9.39 (18)° and adopt a near-to-eclipsed conformation characterized by the torsion angle C(1)—$Cg$(1)—$Cg$(2)—C(6) of -5.6 (2)°, where $Cg$(1) and $Cg$(2) are the centroids of the Cp rings C(1–5) and C(6–10), respectively. The iron—$Cg$ distances in I are: Fe1—$Cg$(1) 1.6399 (14) Å and Fe1—$Cg$(2) 1.6463 (14) Å. The aliphatic bridge assumes a pseudoenvelope conformation and its C═O bond (C11—O 1.2012 (4) Å) is displaced above its bonding Cp ring, the angle subtended by the C?O vector and the Cp ring being 22.5 (2)°.

### Experimental

The title compound was synthesized by acylation of ferrocene with acryloyl chloride in the presence of $AlCl_3$ (Turbitt & Watts, 1972) and characterized by $^1H$ and $^{13}C\{^1H\}$ NMR spectra. Orange-red crystals suitable for X-ray diffraction analysis were obtained by liquid-phase diffusion of hexane into a solution of the compound in dichloromethane.

### Refinement

All H-atoms were included in calculated positions and refined with d(C—H) = 0.93 Å (aromatic) and 0.97 Å (methylene) and $U_{iso}$(H) = 1.2$U_{eq}$(C).
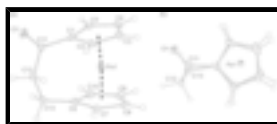
### Figures



Fig. 1. Side (*a*) and top (*b*) views of I showing the atom numbering scheme and displacement ellipsoids for the non-H atoms at the 30% probability level.

# supplementary materials

## [3]ferrocenophan-1-one

*Crystal data*

| | |
|---|---|
| [Fe($C_{13}H_{12}O$)] | $F_{000} = 496$ |
| $M_r = 240.08$ | $D_x = 1.651$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation<br>$\lambda = 0.71073$ Å |
| Hall symbol: -P 2ybc | Cell parameters from 2391 reflections |
| $a = 5.77450$ (10) Å | $\theta = 0.4–27.5º$ |
| $b = 7.3303$ (2) Å | $\mu = 1.52$ mm$^{-1}$ |
| $c = 22.8596$ (6) Å | $T = 150$ (2) K |
| $\beta = 93.242$ (2)º | Block, orange–red |
| $V = 966.07$ (4) Å$^3$ | $0.38 \times 0.30 \times 0.28$ mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Nonius KappaCCD diffractometer | 2223 independent reflections |
| Radiation source: fine-focus sealed tube | 2102 reflections with $I > 2\sigma(I)$ |
| Monochromator: horizontal graphite crystal | $R_{int} = 0.032$ |
| Detector resolution: 9.091 pixels mm$^{-1}$ | $\theta_{max} = 27.5º$ |
| $T = 150(2)$ K | $\theta_{min} = 1.8º$ |
| $\omega$ and $\pi$ scans to fill the Ewald sphere | $h = -7\rightarrow7$ |
| Absorption correction: multi-scan (SORTAV; Blessing, 1995) | $k = -9\rightarrow9$ |
| $T_{min} = 0.579$, $T_{max} = 0.660$ | $l = -29\rightarrow29$ |
| 13397 measured reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.038$ | H-atom parameters constrained |
| $wR(F^2) = 0.096$ | $w = 1/[\sigma^2(F_o^2) + 2.5298P]$<br>where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.31$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 2223 reflections | $\Delta\rho_{max} = 0.53$ e Å$^{-3}$ |
| 136 parameters | $\Delta\rho_{min} = -0.38$ e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none |

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against all reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on all data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

|       | *x*          | *y*         | *z*           | $U_{iso}$*/$U_{eq}$ |
|-------|--------------|-------------|---------------|---------------------|
| Fe1   | 0.18818 (7)  | 0.12608 (6) | 0.151598 (17) | 0.01753 (13)        |
| O1    | 0.6106 (4)   | 0.4906 (4)  | 0.09480 (11)  | 0.0324 (5)          |
| C1    | 0.3394 (5)   | 0.3716 (4)  | 0.15759 (12)  | 0.0187 (5)          |
| C2    | 0.1123 (5)   | 0.3776 (4)  | 0.18047 (12)  | 0.0206 (6)          |
| H2    | −0.0117      | 0.4491      | 0.1664        | 0.025*              |
| C3    | 0.1121 (6)   | 0.2545 (4)  | 0.22849 (13)  | 0.0246 (6)          |
| H3    | −0.0127      | 0.2324      | 0.2515        | 0.029*              |
| C4    | 0.3337 (6)   | 0.1708 (4)  | 0.23551 (13)  | 0.0263 (7)          |
| H4    | 0.3781       | 0.0837      | 0.2635        | 0.032*              |
| C5    | 0.4752 (5)   | 0.2428 (4)  | 0.19256 (13)  | 0.0226 (6)          |
| H5    | 0.6293       | 0.2122      | 0.1877        | 0.027*              |
| C6    | 0.1582 (5)   | 0.0986 (4)  | 0.06275 (12)  | 0.0212 (6)          |
| C7    | −0.0636 (5)  | 0.0829 (4)  | 0.08711 (13)  | 0.0228 (6)          |
| H7    | −0.1912      | 0.1573      | 0.0782        | 0.027*              |
| C8    | −0.0570 (5)  | −0.0656 (4) | 0.12733 (14)  | 0.0242 (6)          |
| H8    | −0.1786      | −0.1044     | 0.1493        | 0.029*              |
| C9    | 0.1688 (6)   | −0.1445 (4) | 0.12808 (14)  | 0.0255 (6)          |
| H9    | 0.2211       | −0.2434     | 0.1506        | 0.031*              |
| C10   | 0.3001 (5)   | −0.0440 (4) | 0.08799 (13)  | 0.0240 (6)          |
| H10   | 0.4530       | −0.0675     | 0.0796        | 0.029*              |
| C11   | 0.4118 (5)   | 0.4452 (4)  | 0.10113 (13)  | 0.0209 (6)          |
| C12   | 0.2345 (6)   | 0.4393 (4)  | 0.04970 (13)  | 0.0238 (6)          |
| H12A  | 0.2733       | 0.5291      | 0.0206        | 0.029*              |
| H12B  | 0.0819       | 0.4680      | 0.0628        | 0.029*              |
| C13   | 0.2334 (6)   | 0.2466 (4)  | 0.02244 (13)  | 0.0250 (6)          |
| H13A  | 0.1303       | 0.2467      | −0.0126       | 0.030*              |
| H13B  | 0.3882       | 0.2189      | 0.0107        | 0.030*              |

*Atomic displacement parameters (Å²)*

|     | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$     | $U^{13}$      | $U^{23}$       |
|-----|------------|------------|------------|--------------|---------------|----------------|
| Fe1 | 0.0204 (2) | 0.0150 (2) | 0.0171 (2) | 0.00020 (17) | −0.00002 (14) | −0.00078 (16)  |

| | | | | | | |
|---|---|---|---|---|---|---|
| O1 | 0.0253 (11) | 0.0364 (14) | 0.0359 (13) | −0.0055 (10) | 0.0037 (9) | 0.0061 (11) |
| C1 | 0.0220 (13) | 0.0145 (12) | 0.0194 (13) | −0.0010 (11) | −0.0012 (10) | −0.0025 (11) |
| C2 | 0.0256 (14) | 0.0172 (13) | 0.0189 (13) | 0.0012 (12) | 0.0003 (11) | −0.0038 (11) |
| C3 | 0.0315 (16) | 0.0269 (16) | 0.0155 (13) | −0.0018 (13) | 0.0037 (11) | −0.0037 (12) |
| C4 | 0.0352 (17) | 0.0240 (15) | 0.0189 (14) | −0.0010 (13) | −0.0057 (12) | 0.0010 (12) |
| C5 | 0.0225 (14) | 0.0201 (14) | 0.0242 (14) | −0.0009 (12) | −0.0066 (11) | −0.0020 (12) |
| C6 | 0.0270 (15) | 0.0193 (14) | 0.0172 (13) | −0.0014 (12) | −0.0002 (11) | −0.0049 (11) |
| C7 | 0.0229 (14) | 0.0241 (15) | 0.0210 (14) | −0.0026 (12) | −0.0032 (11) | −0.0039 (11) |
| C8 | 0.0260 (15) | 0.0204 (14) | 0.0263 (15) | −0.0068 (12) | 0.0016 (12) | −0.0038 (12) |
| C9 | 0.0358 (17) | 0.0123 (13) | 0.0284 (15) | −0.0008 (12) | 0.0008 (13) | −0.0013 (12) |
| C10 | 0.0268 (15) | 0.0198 (14) | 0.0258 (15) | 0.0018 (12) | 0.0051 (12) | −0.0057 (12) |
| C11 | 0.0255 (15) | 0.0132 (13) | 0.0241 (14) | −0.0009 (11) | 0.0016 (11) | 0.0003 (11) |
| C12 | 0.0294 (16) | 0.0217 (14) | 0.0199 (14) | −0.0035 (12) | −0.0011 (12) | 0.0042 (12) |
| C13 | 0.0335 (16) | 0.0252 (15) | 0.0164 (13) | −0.0027 (13) | 0.0036 (12) | −0.0028 (12) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Fe1—C1 | 2.002 (3) | C4—H4 | 0.9300 |
| Fe1—C2 | 2.015 (3) | C5—H5 | 0.9300 |
| Fe1—C7 | 2.036 (3) | C6—C10 | 1.430 (4) |
| Fe1—C6 | 2.039 (3) | C6—C7 | 1.430 (4) |
| Fe1—C5 | 2.045 (3) | C6—C13 | 1.503 (4) |
| Fe1—C10 | 2.048 (3) | C7—C8 | 1.424 (4) |
| Fe1—C8 | 2.049 (3) | C7—H7 | 0.9300 |
| Fe1—C9 | 2.056 (3) | C8—C9 | 1.425 (4) |
| Fe1—C3 | 2.063 (3) | C8—H8 | 0.9300 |
| Fe1—C4 | 2.076 (3) | C9—C10 | 1.427 (4) |
| O1—C11 | 1.212 (4) | C9—H9 | 0.9300 |
| C1—C2 | 1.440 (4) | C10—H10 | 0.9300 |
| C1—C5 | 1.441 (4) | C11—C12 | 1.515 (4) |
| C1—C11 | 1.480 (4) | C12—C13 | 1.544 (4) |
| C2—C3 | 1.421 (4) | C12—H12A | 0.9700 |
| C2—H2 | 0.9300 | C12—H12B | 0.9700 |
| C3—C4 | 1.420 (5) | C13—H13A | 0.9700 |
| C3—H3 | 0.9300 | C13—H13B | 0.9700 |
| C4—C5 | 1.415 (4) | | |
| C1—Fe1—C2 | 42.00 (12) | C4—C3—H3 | 125.6 |
| C1—Fe1—C7 | 118.70 (12) | C2—C3—H3 | 125.6 |
| C2—Fe1—C7 | 102.70 (12) | Fe1—C3—H3 | 127.7 |
| C1—Fe1—C6 | 99.73 (12) | C5—C4—C3 | 108.2 (3) |
| C2—Fe1—C6 | 114.13 (12) | C5—C4—Fe1 | 68.73 (17) |
| C7—Fe1—C6 | 41.09 (12) | C3—C4—Fe1 | 69.44 (17) |
| C1—Fe1—C5 | 41.70 (11) | C5—C4—H4 | 125.9 |
| C2—Fe1—C5 | 69.68 (12) | C3—C4—H4 | 125.9 |
| C7—Fe1—C5 | 157.51 (13) | Fe1—C4—H4 | 127.5 |
| C6—Fe1—C5 | 121.23 (12) | C4—C5—C1 | 108.2 (3) |
| C1—Fe1—C10 | 116.24 (12) | C4—C5—Fe1 | 71.13 (17) |
| C2—Fe1—C10 | 150.81 (12) | C1—C5—Fe1 | 67.56 (16) |
| C7—Fe1—C10 | 68.43 (12) | C4—C5—H5 | 125.9 |

| | | | |
|---|---|---|---|
| C6—Fe1—C10 | 40.96 (12) | C1—C5—H5 | 125.9 |
| C5—Fe1—C10 | 107.44 (13) | Fe1—C5—H5 | 126.9 |
| C1—Fe1—C8 | 158.01 (12) | C10—C6—C7 | 106.8 (3) |
| C2—Fe1—C8 | 123.82 (13) | C10—C6—C13 | 126.6 (3) |
| C7—Fe1—C8 | 40.80 (12) | C7—C6—C13 | 126.4 (3) |
| C6—Fe1—C8 | 69.15 (12) | C10—C6—Fe1 | 69.86 (16) |
| C5—Fe1—C8 | 160.19 (13) | C7—C6—Fe1 | 69.36 (16) |
| C10—Fe1—C8 | 68.35 (13) | C13—C6—Fe1 | 121.9 (2) |
| C1—Fe1—C9 | 154.45 (13) | C8—C7—C6 | 108.7 (3) |
| C2—Fe1—C9 | 163.46 (13) | C8—C7—Fe1 | 70.09 (17) |
| C7—Fe1—C9 | 68.57 (13) | C6—C7—Fe1 | 69.55 (16) |
| C6—Fe1—C9 | 69.15 (12) | C8—C7—H7 | 125.6 |
| C5—Fe1—C9 | 123.64 (13) | C6—C7—H7 | 125.6 |
| C10—Fe1—C9 | 40.68 (12) | Fe1—C7—H7 | 126.3 |
| C8—Fe1—C9 | 40.64 (13) | C7—C8—C9 | 108.0 (3) |
| C1—Fe1—C3 | 69.18 (12) | C7—C8—Fe1 | 69.11 (17) |
| C2—Fe1—C3 | 40.77 (12) | C9—C8—Fe1 | 69.95 (17) |
| C7—Fe1—C3 | 120.66 (13) | C7—C8—H8 | 126.0 |
| C6—Fe1—C3 | 152.09 (12) | C9—C8—H8 | 126.0 |
| C5—Fe1—C3 | 67.99 (13) | Fe1—C8—H8 | 126.5 |
| C10—Fe1—C3 | 166.86 (13) | C8—C9—C10 | 107.6 (3) |
| C8—Fe1—C3 | 111.49 (13) | C8—C9—Fe1 | 69.41 (17) |
| C9—Fe1—C3 | 130.67 (13) | C10—C9—Fe1 | 69.35 (17) |
| C1—Fe1—C4 | 69.06 (12) | C8—C9—H9 | 126.2 |
| C2—Fe1—C4 | 68.71 (12) | C10—C9—H9 | 126.2 |
| C7—Fe1—C4 | 158.22 (13) | Fe1—C9—H9 | 126.6 |
| C6—Fe1—C4 | 160.60 (13) | C9—C10—C6 | 108.9 (3) |
| C5—Fe1—C4 | 40.15 (12) | C9—C10—Fe1 | 69.97 (17) |
| C10—Fe1—C4 | 128.66 (13) | C6—C10—Fe1 | 69.17 (16) |
| C8—Fe1—C4 | 126.57 (13) | C9—C10—H10 | 125.6 |
| C9—Fe1—C4 | 114.02 (13) | C6—C10—H10 | 125.6 |
| C3—Fe1—C4 | 40.13 (13) | Fe1—C10—H10 | 126.9 |
| C2—C1—C5 | 107.3 (3) | O1—C11—C1 | 121.3 (3) |
| C2—C1—C11 | 127.8 (3) | O1—C11—C12 | 121.2 (3) |
| C5—C1—C11 | 123.4 (3) | C1—C11—C12 | 117.0 (3) |
| C2—C1—Fe1 | 69.48 (17) | C11—C12—C13 | 109.1 (3) |
| C5—C1—Fe1 | 70.74 (17) | C11—C12—H12A | 109.9 |
| C11—C1—Fe1 | 114.28 (19) | C13—C12—H12A | 109.9 |
| C3—C2—C1 | 107.6 (3) | C11—C12—H12B | 109.9 |
| C3—C2—Fe1 | 71.43 (18) | C13—C12—H12B | 109.9 |
| C1—C2—Fe1 | 68.51 (17) | H12A—C12—H12B | 108.3 |
| C3—C2—H2 | 126.2 | C6—C13—C12 | 114.1 (2) |
| C1—C2—H2 | 126.2 | C6—C13—H13A | 108.7 |
| Fe1—C2—H2 | 125.4 | C12—C13—H13A | 108.7 |
| C4—C3—C2 | 108.7 (3) | C6—C13—H13B | 108.7 |
| C4—C3—Fe1 | 70.44 (17) | C12—C13—H13B | 108.7 |
| C2—C3—Fe1 | 67.80 (16) | H13A—C13—H13B | 107.6 |

**Fig. 1**