

A practical synthesis of ethynylferrocene from ferrocene carboxaldehyde: structure of 1,4-diferrocenyl-1,3-butadiyne

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Abstract

Ethynylferrocene was satisfactorily obtained by a Wittig reaction between ferrocene carboxaldehyde and chloromethyltriphenylphosphonium ylid to give an *E/Z* mixture of 2-chloro-1-ferrocenylethene. Both isomers were isolated pure by chemical methods. Reaction of the isomers mixture with *n*-butyllithium allowed ethynylferrocene to be obtained in good yield. The method was applied in one pot giving the ethynylferrocene and (*E/Z*)-1,4-diferrocenyl-but-1-en-3-yne as a secondary product. Oxidative coupling to 1,4-diferrocenyl-1,3-butadiyne has been carried out in quantitative yields. A single-crystal analysis of the diyne was carried out, but the compound is unreactive in solid state.

Keywords: Ferrocenes; Dienes; Wittig reaction; Synthesis; X-ray crystal structure

1. Introduction

Compounds containing ferrocene have been used in electrochemistry [1], as molecular sensors [2,3], as molecular ferromagnets [4,5], and in nonlinear optics [6,7]. It is now well established that molecular structures with differences between ground-state and excited-state dipole moments and large transition dipole moments have large second-order nonlinearities [8]. Molecules with π donor–acceptor interactions are promising candidates. The vinylferrocene moiety has been used as a π -electron donor in several compounds [9], with high second harmonic generation (SHG) [10] efficiencies.

Ethynylferrocene was synthesized for the polymerization studies and for dimerization to 1,4-diferrocenyl-1,3-butadiyne for topopolymerization to prepare electroactive and nonlinear-optic materials.

2. Discussion

2.1. Synthesis of ethynylferrocene

Synthesis of ethynylferrocene was by hydrochloric acid elimination from 2-chloro-1-ferrocenylethene,

Scheme 1. In this way, (*E/Z*)-2-chloro-1-ferrocenylethene, (*E/Z*)-1, was previously prepared by treatment of chloroacetylferrocene with Al_2O_3 in toluene in low yields [11].

However, synthesis of (*E/Z*)-1 was carried in satisfactory yield by the Wittig reaction between the chloromethyltriphenylphosphonium ylid and ferrocenyl carboxaldehyde. The ratio of *E* and *Z* isomers in THF depends on the base used in the preparation of the ylid. With *n*-butyllithium, with 67% yield, *E/Z* was 1:3. In this reaction, (*E/Z*)-1-ferrocenyl-1-pentene was isolated as a deep orange oil, as a minor product. With KO^tBu in 92% yield, *E/Z* was 46:54.

Both isomers have been isolated pure by stereospecific reaction with the appropriate base, for unequivocal identification and for use in homocoupling reactions.

The mixture of (*E/Z*)-1 was treated with 1 equivalent of KO^tBu in toluene at room temperature with specific *Z*-dehydrochlorination, giving ethynylferrocene and the (*E*)-isomer pure as an orange solid, m.p. 41–43°C. Two equivalents of phenyllithium in diethyl ether at 0°C with specific *E*-dehydrochlorination give ethynylferrocene and the (*Z*)-isomer pure, as an orange solid, m.p. 47–48°C. The first elimination involves an *E2* mechanism and the second an *Ecb2* [12].

The above two consecutive reactions were carried out in a pot using KO^tBu in toluene at reflux tempera-

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ture. Two products were isolated: (*E/Z*)-1,4-diferrocenyl-but-1-en-3-yne, **4**, (21%), as a 1 : 1 mixture, and the acetylene **2** in 45% yield, Scheme 2.

The *E/Z* mixture of **4** was separated by column chromatography and the (*Z*)-isomer as an orange-red solid, m.p. 110–111°C and the (*E*)-isomer, as an orange-red solid, m.p. 190°C (dec.).

The formation of (*E/Z*)-**4**, takes place after partial conversion of (*E/Z*)-**1** to give the acetylene **2**. Subsequent reaction with base, gives the acetylide for addition-elimination with (*E/Z*)-**1**, Scheme 3.

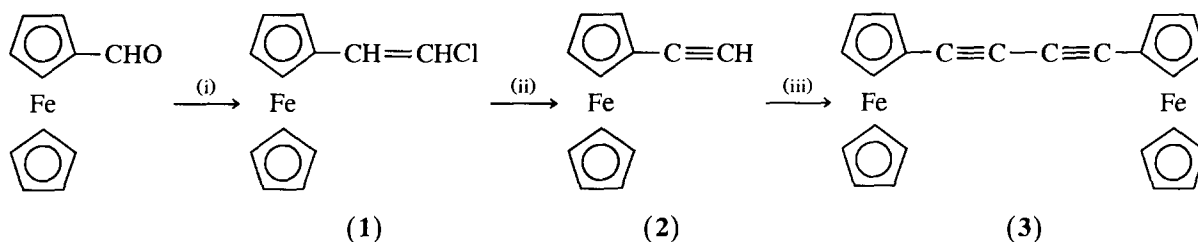
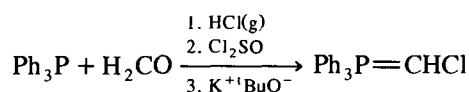
Both (*E*)- and (*Z*)-**4** were well identified by spectral analysis. The mass spectra gave the molecular formula $C_{24}H_{20}Fe_2$ and the NMR spectra showed the olefinic protons H_A at 6.44 (6.76 ppm) and H_X at 5.59 (5.88 ppm) with $J = 11.4$ ($J = 16.0$ Hz) for the *Z*- (*E*-isomer).

2.2. Synthesis of 1,4-diferrocenyl-1,3-butadiyne, **3**

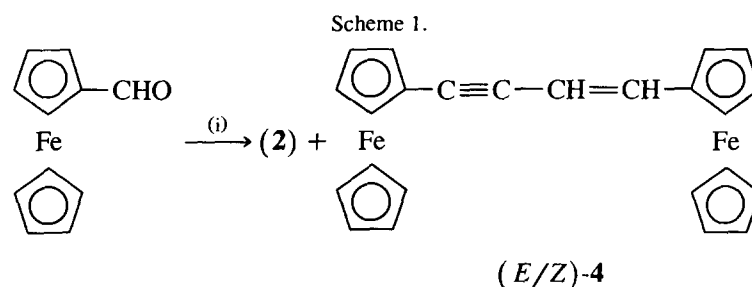
Synthesis of **3** was carried out in good yield by oxidative homocoupling reaction from acetylene **2** in pyridine and in air, in the presence of copper(I) chloride.

2.3. Molecular structure of 1,4-diferrocenyl-1,3-butadiyne, **3**

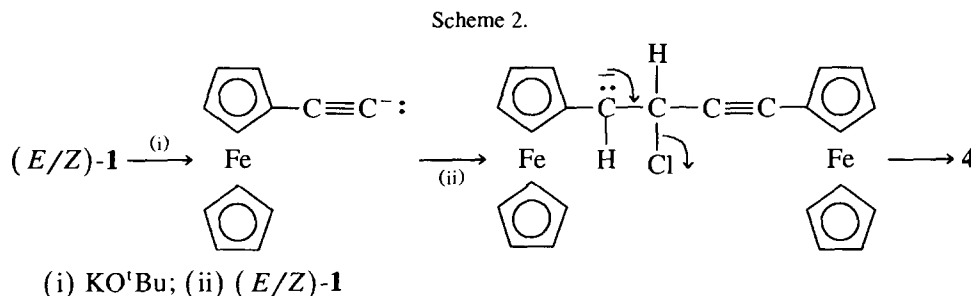
The molecular structure of 1,4-diferrocenyl-1,3-butadiyne is shown in Fig. 1. The relevant atomic coordinates, and bond distances and angles are listed in Tables 1–3. The structure consists of a 1,3-butadiyne linear chain containing two ferrocenyl substituents in positions 1 and 4 of the chain, each ferrocenyl moiety on opposite sides of the mean plane of the chain and Cp ring, with a symmetry centre in C1–C1A of the chain



(i), $Ph_3P=CHCl$; (ii) $KOtBu$; (iii) $Cu_2Cl_2/O_2/Py$



(i) $[Ph_3PCH_2Cl]Cl-KOtBu$



(i) $KOtBu$; (ii) (*E/Z*)-**1**

Scheme 3.

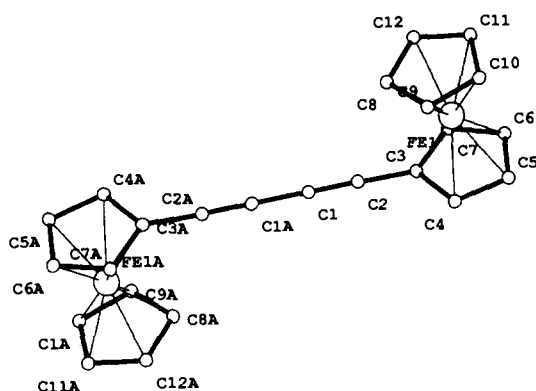


Fig. 1. PLUTO [13] view of the molecule showing the atomic numbering.

Table 1
Atomic parameters for $C_{24}H_{18}Fe_2$

Atom	x	y	z	U_{eq}
FE1	0.84705(2)	0.18560(3)	0.29715(4)	340(1)
C1	0.55702(24)	0.01275(28)	0.02302(38)	590(9)
C2	0.65644(22)	0.03512(26)	0.06363(35)	550(8)
C3	0.77520(20)	0.05916(23)	0.10684(30)	467(7)
C4	0.85206(20)	-0.00895(23)	0.23884(34)	461(7)
C5	0.96118(20)	0.04619(25)	0.24094(36)	501(8)
C6	0.95368(22)	0.14737(27)	0.11263(34)	525(8)
C7	0.83968(24)	0.15696(27)	0.03009(32)	507(8)
C8	0.71636(22)	0.26044(26)	0.41178(33)	506(8)
C9	0.79818(26)	0.20464(27)	0.54416(33)	545(9)
C10	0.90257(24)	0.27028(29)	0.53928(34)	569(8)
C11	0.88467(25)	0.36600(25)	0.40430(36)	558(8)
C12	0.77002(24)	0.36004(25)	0.32586(34)	516(8)

Coordinates and thermal parameters as $U_{eq} = (1/3)\sum[U_{ij} \cdot a_i^* \cdot a_j^* \cdot a_i \cdot a_j \cdot \cos(a_i, a_j)] \times 10^4$.

Table 2
Bond distances for $C_{24}H_{18}Fe_2$

Fe1–C01	1.645(1)	C5–C6	1.411(4)
Fe1–C02	1.650(1)	C6–C7	1.410(4)
C1–C1A	1.373(3)	C8–C9	1.411(4)
C1–C2	1.198(4)	C8–C12	1.407(4)
C2–C3	1.422(3)	C9–C10	1.413(4)
C3–C4	1.433(3)	C10–C11	1.407(4)
C3–C7	1.430(4)	C11–C12	1.406(4)
C4–C5	1.410(3)		

Table 3
Bond angles for $C_{24}H_{18}Fe_2$

C2–C1–C1A	179.8(3)	C5–C6–C7	108.5(2)
C1–C2–C3	178.1(3)	C3–C7–C6	107.8(2)
C2–C3–C7	126.7(2)	C9–C8–C12	108.0(2)
C2–C3–C4	126.0(2)	C8–C9–C10	107.9(2)
C4–C3–C7	107.3(2)	C9–C10–C11	107.8(2)
C3–C4–C5	107.9(2)	C10–C11–C12	108.2(2)
C4–C5–C6	108.4(2)	C8–C12–C11	108.1(2)

that coincides with the crystallographic centre of symmetry. The Cp rings in the ferrocene unit are eclipsed and, as expected both are planar. When C1 and C2 in the substituted cyclopentadienyl deviate by 0.014(3) and $-0.013(3)$ Å from the mean plane. The bonds and angles between the Cp rings are as follows: Fe to the centroids of the Cp rings are 1.645(1) and 1.650(1) Å, while Fe–C distances range between 2.026(2) to 2.051(3) Å, comparable with those found in ferrocene [14]. The Cp rings in the ferrocenyl unit are planar with a dihedral angle of 3.1(1)°.

The C–C distances in Cp rings vary from 1.406(4) to 1.433(3) Å and the C–C–C angles range between 107.3(2) and 108.5(2)°. The angles C2–C1–C1A = 179.8, C1–C2–C3 = 178.1(3)° are almost linear and the angles C2–C3–C7 = 126.7(2) and C2–C3–C4 = 126.0(2)° are larger than 120°. Both sets of values are similar to those for other ferrocenyl compounds [14,15]. The acetylide bond C1–C2 = 1.198(4) and C1–C1A = 1.373(3) Å are of the order of those observed in other acetylides [16].

The molecules pack in zig-zag chains along the *b* direction with contacts of 5.03 Å between the centroids of rings, and the ferrocenyl units on adjacent chains [17] make angles of 83°, Fig. 2 [13].

3. Experimental

3.1. Synthesis of ethynylferrocene

3.1.1. Preparation of 2-chloro-1-ferrocenylethene 1

To a suspension of chloromethyltriphenylphosphonium chloride (1.633 g, 4.9 mmol) in dry THF (4 ml) under argon of 0°C was added: (a) *n*-butyllithium (3.15 ml of 1.6 M solution in hexane, 5 mmol) or (b) potassium *tert*-butoxide (0.6 g, 4.9 mmol). The mixture turned orange and after 15 min a solution of 1.05 g (4.9

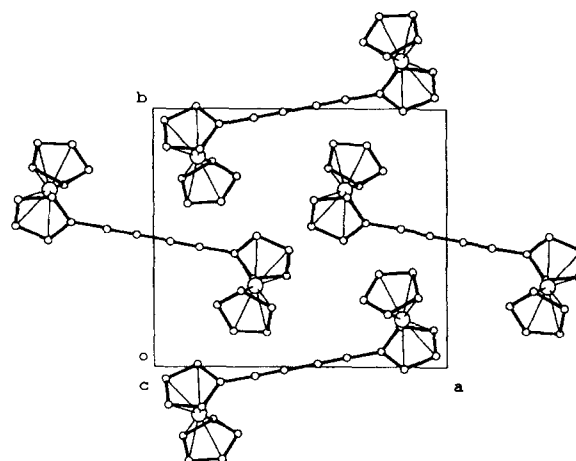


Fig. 2. Packing of the molecules viewed down the *c* axis.

mmol) of ferrocenylcarboxaldehyde in dry THF (4 ml) was added dropwise. The mixture was allowed to warm to room temperature. After 15 h the solvent was removed under vacuum. The residual solid was extracted (3 × 5 ml) and the extract was concentrated and purified by chromatography on silica gel using hexane-dichloromethane (4:1) as eluant. 2-Chloro-1-ferrocenylethene, **1**, was obtained as an orange oil, consisting of a mixture of *E* and *Z* isomers. Yield with base (a) 0.77 g, 67%, (*E/Z*, 1:3 by NMR spectroscopy); yield with base (b) 1.11 g, 92%, *E/Z*, 46:54, by NMR spectroscopy). The isomers were separated chemically.

Separation of (*E*)-1. A mixture of (*E/Z*)-**1** (46:54), 0.5 g, was treated with 0.31 g of potassium *tert*-butoxide in toluene, 5 ml, at room temperature for 3 h. Selective dehydrochlorination of the (*Z*)-isomer was complete (thin layer chromatography). After silica gel column chromatography (hexane-dichloromethane 4:1), the (*E*)-isomer was isolated as a pure orange solid, 0.22 g (96%), m.p. 41–43°C, together with ethynylferrocene, 0.21 g (91%).

Separation of (*Z*)-1. A mixture of (*E/Z*)-**1** (*E/Z*, 46:54), 0.5 g, was treated with 0.16 g of phenyllithium, in diethyl ether 10 ml at 0°C for 3 h. Selective dehydrochlorination of the (*E*)-**1** isomer was complete (thin layer chromatography). After silica gel column chromatography (hexane-dichloromethane 4:1), the (*Z*)-**1** isomer was isolated pure as an orange solid, 0.225 g (98%), m.p. 47–48°C, together with ethynylferrocene, 0.22 g (96%).

Spectral data for *E*-1 and *Z*-1 isomers. Anal. Found: C, 58.31; H, 4.65; Cl, 14.15. C₁₂H₁₁FeCl. Calc.: C, 58.46; H, 4.50; Cl, 14.38%. IR (film): 3085 (br. C–H st., Cp and vinyl), 1610 (C=C), 1410, 1005, 820 (ferrocene), 930 (=CH bending, in *E*-isomer), 710 (=CH tendency, in *Z*-isomer). ¹H NMR (CDCl₃): 4.16 (s, 5H, Cp), 4.30 (t, 2H, *J* = 1.8 Hz, H-3, H-4), 4.70 (t, 2H, *J* = 1.8 Hz, H-2, H-5, in *Z*-isomer), 4.24 (t, 2H, *J* = 1.8 Hz, H-2, H-5, in *E*-isomer), 6.07 (d, 1H, *J* = 7.8 Hz, O=CHCl, in *Z*-isomer), 6.20 (d, 1H, *J* = 13.5 Hz, C=CHCl, in *E*-isomer), 6.38 (d, 1H, *J* = 7.8 Hz, Cp–CH=, *Z*-isomer), 6.57 (d, 1H, *J* = 13.5 Hz, Cp–CH=, in *E*-isomer). ¹³C NMR (CDCl₃): 66.5 (C-2, C-5, in *E*-isomer), 69.8 (C-2, C-5, in *Z*-isomer), 69.0 (C-3, C-4), 69.3 (Cp), 71.7 (C-1, in *Z*-isomer), 80.6 (C-1, in *E*-isomer), 113.9 (=CH–Cp, *E*-isomer), 114.3 (=CH–Cp, *Z*-isomer), 128.0 (=CHCl, *Z*-isomer), 130.8 (=CHCl, *E*-isomer).

3.2. Synthesis of ethynylferrocene, **2**

To a solution of 0.664 g (2.7 mmol) of a mixture of *E/Z*-**1** in 5 ml of dry toluene were added 0.33 g (2.7

mmol) of potassium *tert*-butoxide at 0°C under argon. The mixture was warmed to reflux temperature for 2 h. After cooling to room temperature, water (5 ml) was added and the mixture extracted with hexane. The solvent was removed under reduced pressure and the residual oil was purified by silica gel column chromatography using hexane-dichloromethane (4:1) as the eluant. Ethynylferrocene was obtained as an orange-red solid, 0.538 g (98%), m.p. 53–54°C [18].

Anal. Found: C, 68.41; H, 4.95. C₁₂H₁₀Fe. Calc.: C, 68.61; H, 4.80%. MS (70 eV): 210 (M⁺, 100), 153 (19), 152 (33), 145 (13), 121 (73), 105 (6), 89 (24), 56 (23). IR (film): 3260 (≡C–H), 3085 (=C–H, ferrocene), 2100 (C≡C, 1410, 1000, 820 (ferrocene), 640 (=C–H)). ¹H-NMR (CDCl₃): 2.70 (s, 1H, =CH), 4.15 (t, 2H, *J* = 1.78 Hz, H-2, H-5), 4.20 (s, 5H, Cp), 4.45 (t, 2H, *J* = 0.78 Hz, H-3, H-4). ¹³C (CDCl₃): 63.7 (C-1), 68.6 (C-2, C-5), 69.9 (Cp), 71.5 (C-3, C-5), 73.9 (=CH), 82.4 (Cp–C=).

3.3. Preparation of ethynylferrocene in a one-pot reaction from ferrocene carboxaldehyde and chloromethylenetriphenylphosphonium ylid

To a suspension of chloromethylenetriphenylphosphonium chloride, 3.3 g (9.5 mmol) in 10 ml of dry toluene cooled in an ice-salt bath was added potassium *tert*-butoxide, 1.2 g (9.8 mmol) with stirring. After 30 min, a solution of ferrocene carboxaldehyde, 1 g (4.6 mmol) in 5 ml of toluene was added dropwise. The mixture was warmed to room temperature and stirred for 24 h. Then, potassium *tert*-butoxide, 3.1 g (25 mmol), was added and the mixture was heated to reflux temperature for 1 h. The solvent was removed under reduced pressure and the residual solid was purified by silica gel column chromatography, using hexane-dichloromethane, 4:1, as the eluant. Three fractions were separated: (i) 410 mg (21%) of (*E/Z*)-1,4-diferrocenylbut-1-en-3-yne (1:1), **4** as an orange solid, which was carefully chromatographed to isolate both isomers as deep orange crystals, (*Z*)-**4**, m.p. 110–111°C and (*E*)-**4**, m.p. 190°C (dec.); (ii) 370 mg (33%) of (*Z*)-**1**, as a red solid, m.p. 47–48°C; (iii) 420 mg (45%) of ethynylferrocene, **2**, as an orange-red solid, m.p. 53–54°C.

Spectral data for *E*-4 and (*Z*)-4. Anal. Found: C, 68.42; H, 5.05; C₂₄H₂₀Fe₂. Calc.: C, 68.61; H, 4.80%. MS (70 eV), *E* and *Z*-isomers; 420 (M⁺, 100%); 298 (11); 234 (6); 210 (11); 186 (16); 121 (16). IR (KBr), *E* and *Z*-isomers; 3095 (=C–H, st), 2195 (C≡C), 1605 (C=C, st), 1410 (ferrocene), 1110, 1060 (br), 1040, 1030, 1002 (ferrocene), 820 (=C–H), 980 (C–C, *E*-isomer) and 760 (C=C, *Z*-isomer).

(*Z*)-**4** isomer: ¹H NMR (CDCl₃): 4.18 (s, 5H, Cp–C_{sp}²), 4.27 (s, 5H, Cp–C_{sp}), 4.51 (t, 2H, *J* = 1.8 Hz, H2, H5), 4.88 (t, 2H, *J* = 1.8 Hz, H3, H4), 4.32 (t, 2H,

$J = 1.8$ Hz, H2', H5'), 4.23 (t, 2H, $J = 1.8$ Hz, H3', H4'), 5.59 (d, 1H, $J = 11.4$ Hz, =CHCp), 6.44 (d, 1H, $J = 11.4$ Hz, CH-C_{sp}).

(E)-4 isomer: ¹H NMR (CDCl₃): 4.18 (s, 5H, Cp-C_{sp2}), 4.26 (s, 5H, Cp-C_{sp}), 4.39 (t, 2H, $J = 1.8$ Hz, H2 and H5), 4.22 (t, 2H, $J = 1.8$ Hz, H3 and H4), 4.44 (t, 2H, $J = 1.8$ Hz, H2' and H5'), 4.40 (t, 2H, $J = 1.8$ Hz, H33' and H4'), 5.88 (d, 1H, $J = 16$ Hz, Cp-CH=), 6.76 (d, 1H, $J = 16$ Hz, C_{sp}-CH=).

3.4. Synthesis of 1,4-diferrocenyl-1,3-butadiyne, 3

A mixture of 180 mg (0.89 mmol) of ethynylferrocene, 9 mg (0.09 mmol) of copper(I) chloride, and 25 ml freshly distilled pyridine was warmed at 50°C in air for 3 h (monitored by thin layer chromatography, hexane-dichloromethane, 3:1). The mixture was cooled and the pyridine removed under reduced pressure, giving a residual solid, which was treated with 20 ml of a saturated solution of ammonium chloride, and extracted with dichloromethane. The organic layer was dried with MgSO₄. The solvent was removed under reduced pressure and 1,4-diferrocenyl-1,3-butadiyne was obtained as a dark red solid, 160 mg (89%), m.p. 194–195°C.

Spectral data for 3. Anal. Found: C, 68.60; H, 4.53. C₂₄H₁₈Fe₂. Calc.: C, 68.95; H, 4.34%. MS (70 eV): 418 (M⁺, 100); 297 (6); 240 (7); 239 (12); 209 (9); 121 (10). ¹H-NMR (CDCl₃): 4.24 (t, $J = 1.7$ Hz, 4H, H-2, H-5, H-1', H-5'); 4.26 (s, 10H, Cp); 4.51 (t, $J = 1.7$ Hz, 4H, H-3, H-4, H-3', H-4'). IR (KBr) cm⁻¹: 3085 (C-H, ferrocene), 2140 (C≡C), 1410 (C=C, ferrocene), 1100, 1000 and 815 (ferrocene, C-H).

3.5. Crystal structure determination of 3

The dark red crystals of 1,4-diferrocenyl-1,3-diyne used for X-ray diffraction were grown by slow evaporation from a dilute toluene solution.

A crystal of 0.41 × 0.32 × 0.37 mm³ dimensions was used for the crystallography. Accurate cell dimensions were determined by least squares analysis of setting angles of 67 reflections ($5 < 2\theta < 50^\circ$), using graphite monochromated Mo K α radiation ($\lambda = 0.7107$ Å) automatically located and centered on a four-circle Philips PW 1100 diffractometer. Monoclinic, space group $P2_1/a$, with $a = 11.859(1)$, $b = 10.228(1)$, $c = 7.544(1)$ Å, $\beta = 98.08(1)^\circ$, $V = 905.9(1)$ Å³. Molecular formula C₂₄H₁₈Fe₂, molecular weight 418.11, $D_c = 1.533(2)$ g cm⁻³, $Z = 4$, $F(000) = 428.0$. Correction by absorption was neglected, $\mu = 16.043$ cm⁻¹. Data collection: two standard reflections were measured every 90 min to ascertain crystal stability; no significant variation was observed. All the reflections were corrected for Lorentz and polarization effects. For the intensity measurement, reflections were surveyed in the range $2 < \theta < 25^\circ$, from 1561 independent reflections measured,

1497 were considered as observed, satisfying the criterion $I > 3\sigma(I)$ in the range $h \pm 14$, k 0/13, l 0/9, and were used in the subsequent calculations.

The crystal structure was partially elucidated by direct methods [19]. After preliminary adjustment of the heavy atoms, H-atoms were positioned from difference Fourier maps. Thereafter, several cycles of full-matrix least squares calculations were carried out with anisotropic thermal parameters for heavy atoms and the H-atoms were included as fixed contributors [20], and convergence was reached at $R = 0.029$ and $R_w = 0.034$ with a weighting scheme [21] to prevent trends in $w\Delta^2 F$ vs. $\langle F_0 \rangle$ and vs. $\langle \sin \theta/\lambda \rangle$. The final difference synthesis showed no peaks exceeding 0.43 e Å⁻³.

The atomic scattering factors and the anomalous dispersion correction were taken from the literature [22]. Atomic coordinates, bond distances and angles were calculated using the PARST program [23]. All relevant data have been deposited at the Cambridge Crystallographic Data Centre.

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