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Propynylferrocene and (phenylethynyl)ferrocene

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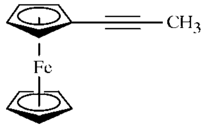
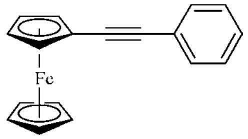
The title compounds, propynylferrocene, $[Fe(C_5H_5)(C_8H_7)]$, (I), and (phenylethynyl)ferrocene, $[Fe(C_5H_5)(C_{13}H_9)]$, (II), are stabilized by weak C—H$\cdots\pi$ interactions. The C$\equiv$C bond distances in these molecules are in the range 1.182 (3)–1.192 (3) Å. In (II), the ferrocenyl and phenyl groups are perpendicular, making an angle of 89.06 (13)°, which is a rare occurrence.

Comment

Recently, alkyne chemistry has experienced a major renaissance due to the involvement of molecules with C$\equiv$C bonds in the frontiers of modern organic chemistry, namely biochemistry, materials science and organometallic chemistry (Stang & Diederich, 1995; Diederich *et al.*, 2005). In this regard, ferrocenylalkynes occupy an important position since they can be converted to a structurally diverse set of ferrocenyl (Fc) compounds that are attractive synthetic targets owing to their physical, chemical and biological properties (Togni & Hayashi, 1995). The Fc group is often incorporated into a bioactive compound to obtain enhanced biological activities (Zora *et al.*, 2002, 2003; Jaouen *et al.*, 2004). In addition, the Fc group is ideal for use in drug design owing to its low toxicity, stability and lipophilicity (Biot *et al.*, 2000).



(I)



(II)

There is considerable interest in the synthesis of new materials with large second-order optical non-linearities because of their potential use in device applications related to telecommunications, optical computing, optical storage and optical information processing (Williams, 1984; Chemla & Zyss, 1987). In this regard, ferrocene-based donor–acceptor chromophores have been investigated widely for their linear and non-linear optical properties (Barlow & Marder, 2000; Stankovic *et al.*, 2001). In particular, ethynylferrocene (Wurst *et al.*, 1995; Polin & Schottenberger, 1996) and its derivatives (Nock & Schottenberger, 1993; Ingham *et al.*, 1994) have attracted substantial interest owing to the potential for electronic communication through the unsaturated alkyne linkage to the Fe center. There are also examples of ethynylferrocene linked through the alkyne spacer group to other metal centers (Berry *et al.*, 2004; Laus *et al.*, 2005). In this respect, the crystal structures of ethynylferrocene (Wurst *et al.*, 1995; Steiner *et al.*, 1996) and its derivatives (Ingham *et al.*, 1994; Dufkova *et al.*, 2003; Hocek *et al.*, 2004) have gained importance. We report here the crystal structures of propynylferrocene, (I), and (phenylethynyl)ferrocene, (II).

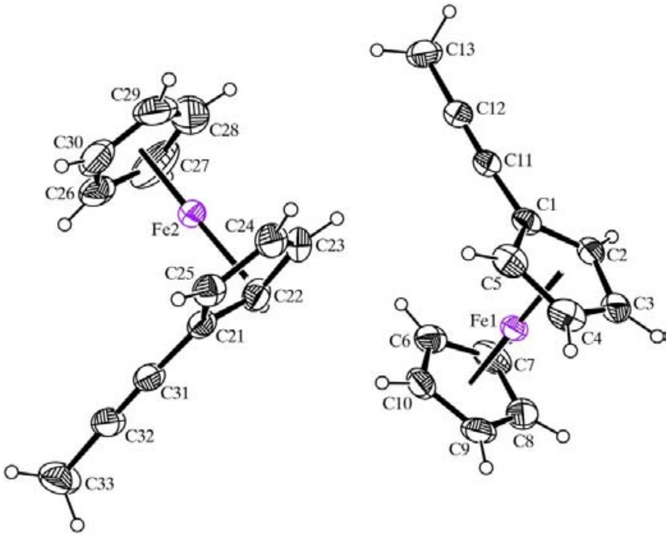


Figure 1
A view of the two molecules of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids.

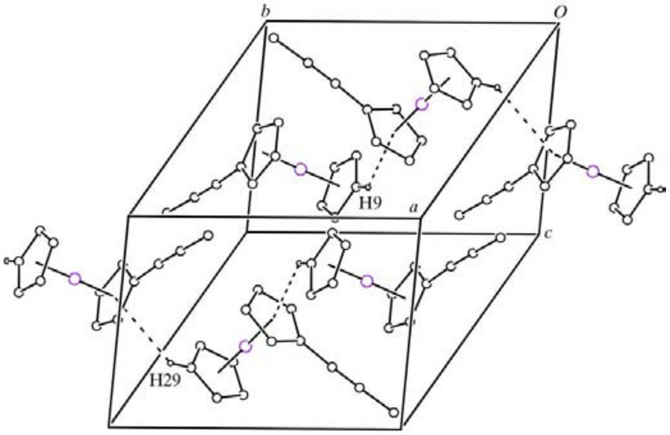


Figure 2
A packing diagram of (I), showing the C—H$\cdots\pi$ interactions as dashed lines. H atoms not involved in C—H$\cdots\pi$ interactions have been omitted for clarity.

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The molecular structure of (I) is shown in Fig. 1. Selected bond distances and angles are given in Table 1. There are two molecules present in the asymmetric unit of (I). The C≡C bond distances in these molecules are 1.182 (3) and 1.184 (3) Å, which are in accord with those in similar complexes, *e.g.* 1,1,3-triferrocenylprop-2-yn-1-ol [1.180 (13) Å; Lucasser *et al.*, 1995] and 1-trimethylsilylethynylferrocene [1.188 (7) Å; Schottenberger *et al.*, 1999]. The Fe—Cg_s and Fe—Cg_{as} distances are in the range 1.6388 (11)–1.6467 (11) Å, and the Cg_s—Fe—Cg_{as} angles are 178.64 (8) and 178.77 (5)°, where Cg_s and Cg_{as} are the substituted and unsubstituted Cp ring centroids. The Cp rings in each molecule are almost parallel since the angles between the Cp ring planes are 1.43 (10) and 1.71 (19)°. The Cp rings of the Fc groups deviate slightly from an eclipsed conformation, as evidenced by the average C—Cg_s—Cg_{as}—C torsion angles of 7.41 (3) and −4.71 (3)°. The C—C bond distances in the Cp rings range from 1.342 (5) to 1.427 (3)°, while the Fe—C bond lengths range between 2.006 (3) and 2.0510 (17)°, all of which are as expected.

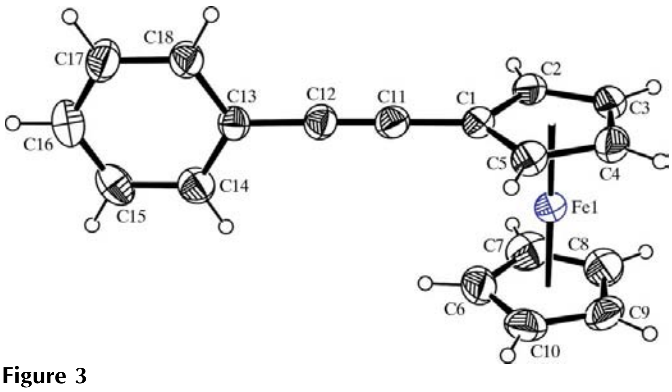

Figure 3
A view of (II), showing the atom-numbering scheme and 50% probability displacement ellipsoids.

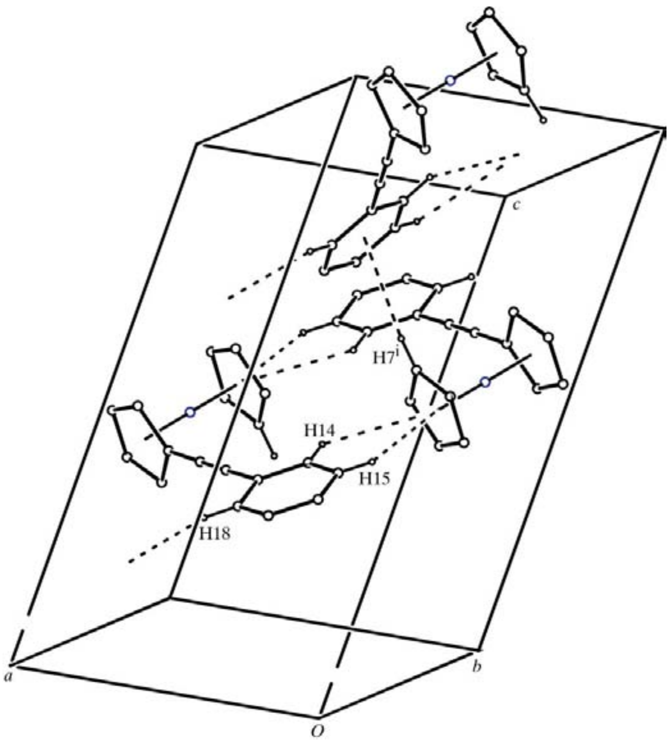

Figure 4
A packing diagram of (II), showing the C—H$\cdots\pi$ interactions as dashed lines. H atoms not involved in C—H$\cdots\pi$ interactions have been omitted for clarity. [Symmetry code: (i) $-x + 1$, $-y + 1$, $-z + 1$.]

As in ethynylferrocene (Wurst *et al.*, 1995; Steiner *et al.*, 1996), there are no direction-specific aromatic π–π interactions between adjacent rings in (I), but there are two C—H$\cdots\pi$ interactions (Table 2 and Fig. 2).

The molecular structure of (II) is shown in Fig. 3. Selected bond distances and angles are given in Table 3. Compound (II) comprises Fc and phenyl rings linked by an acetylene residue. The unusual feature of (II) is that the substituted Cp and phenyl rings are almost perpendicular, with an angle of 89.06 (13)°, which is a rare occurrence. This is clearly an indication of the interrupted conjugation between the Fc and Ph groups. However, in 1,1′-bis(phenylethynyl)ferrocene (Ingham *et al.*, 1994), a closely related compound, there is not a large tilting of the phenyl groups from the planes of the cyclopentadienyl rings since the angles between the phenyl rings and the cyclopentadienyl rings are 11.2 (2) and 26.6 (2)°. Moreover, a literature search for crystal structures incorporating the diphenylacetylene group has revealed some derivatives, *viz.* tolane (Mavridis & Moustakali-Mavridis, 1977), perfluorodiphenylacetylene (Goodhand & Hamor, 1979), octafluoronaphthalene–diphenylacetylene (1/1) (Collings *et al.*, 2001) and *N*-[4-(phenylethynyl)phenyl]benzamide (Yin *et al.*, 2005). In all, ethynyl-bridged phenyl rings are found to be almost coplanar, which is in contrast to the situation in (II).

The C≡C bond length in (II) is 1.192 (3) Å, which is in agreement with those in 1,1′-bis(phenylethynyl)ferrocene (Ingham *et al.*, 1994) and (*Z*)-1,4-diferrocenylbut-1-en-3-yne [1.199 (4) Å; Wurst *et al.*, 1995]. The Fc group is almost in an eclipsed conformation since the average C11—Cg_s—Cg_{as}—C6 pseudo-torsion angle is 0.60 (4)°. The centroids of the Cp rings are almost equidistant from Fe atoms, as indicated by the Fe—Cg_s and Fe—Cg_{as} distances of 1.641 (12) and 1.642 (12) Å, respectively. The Cg_s—Fe—Cg_{as} angle is 179.16 (6)°. The Cp rings are almost parallel since the angle between the Cp ring planes is 1.62 (16)°. The C—C bond distances in the Cp rings range from 1.390 (4) to 1.428 (3) Å. The Fe—C bond lengths are in the range 2.021 (3)–2.039 (2) Å.

As in compound (I) and ethynylferrocene (Wurst *et al.*, 1995; Steiner *et al.*, 1996), compound (II) is also stabilized by four C—H$\cdots\pi$ interactions, two of them, C14—H14$\cdots\pi$ and C15—H15$\cdots\pi$, in the chelate ring form (Table 4 and Fig. 4).

Experimental

Compound (I) was prepared from ethynylferrocene by the Vilsmeier–Haack formylation (Doisneau *et al.*, 1992). Suitable crystals of (I) were obtained by slow evaporation of a 19:1 hexane–ethyl acetate solution at room temperature. Compound (II) was synthesized by a modified literature procedure (Okuro *et al.*, 1993). Iodobenzene

(0.3 ml, 2.38 mmol) and ethynylferrocene (500 mg, 2.38 mmol) were added to a mixture of CuI (23 mg, 0.12 mmol), PPh_3 (62 mg, 0.24 mmol), K_2CO_3 (493 mg, 3.57 mmol) and dimethylformamide (4.8 ml) under argon. The resulting mixture was refluxed at 393 K for 16 h. The solution was then extracted with ether, washed with water and dried over $MgSO_4$. Final purification was achieved by flash column chromatography on silica gel using hexane as the eluant. The product was obtained in 47% yield. The spectroscopic data for (II) were in agreement with those reported previously for this compound (Stepnicka *et al.*, 1999). Single crystals of (II) were obtained by slow evaporation of a 19:1 hexane–ethyl acetate solution at room temperature.

Compound (I)

Crystal data

$[Fe(C_5H_5)(C_8H_7)]$
$M_r = 224.08$
Triclinic, $P\bar{1}$
$a = 9.8232$ (7) Å
$b = 10.3192$ (7) Å
$c = 11.1465$ (8) Å
$\alpha = 76.431$ (5)°
$\beta = 86.740$ (6)°
$\gamma = 70.527$ (5)°
$V = 1035.25$ (13) Å^3
$Z = 4$
$D_x = 1.437$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.41$ mm^{-1}
$T = 296$ (2) K
Prism, red
0.60 × 0.49 × 0.40 mm

Data collection

Stoe IPDS-II diffractometer
ω scan
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{\min} = 0.558$, $T_{\max} = 0.670$
15013 measured reflections
4072 independent reflections
3613 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.046$
$\theta_{\max} = 26.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.074$
$S = 1.01$
4072 reflections
255 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.2017P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

C1—C11	1.429 (3)	C21—C31	1.427 (3)
C11—C12	1.184 (3)	C31—C32	1.182 (3)
C12—C13	1.464 (3)	C32—C33	1.461 (3)
C5—C1—C2	107.29 (17)	C22—C21—C31	125.93 (18)
C2—C1—C11	126.30 (17)	C25—C21—C31	126.5 (2)
C12—C11—C1	176.28 (19)	C32—C31—C21	177.5 (2)
C11—C12—C13	178.9 (2)	C31—C32—C33	178.9 (2)
C11—C1—C2—C3	177.69 (17)	C31—C21—C22—C23	−178.92 (18)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

*Cg*1 and *Cg*2 are the centroids of the C1–C5 and C21–C25 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9···*Cg*2$^{\rm i}$	0.93	3.10	3.874 (2)	142
C29—H29···*Cg*1$^{\rm ii}$	0.93	3.12	3.889 (3)	141

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y, -z+1$.

Compound (II)

Crystal data

$[Fe(C_5H_5)(C_{13}H_9)]$
$M_r = 286.14$
Monoclinic, $P2_1/c$
$a = 8.7368$ (9) Å
$b = 10.6296$ (15) Å
$c = 15.1113$ (16) Å
$\beta = 105.327$ (8)°
$V = 1353.5$ (3) Å^3
$Z = 4$
$D_x = 1.404$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.10$ mm^{-1}
$T = 296$ (2) K
Plate, red
0.62 × 0.51 × 0.14 mm

Data collection

Stoe IPDS-II diffractometer
ω scan
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{\min} = 0.583$, $T_{\max} = 0.848$
7479 measured reflections
2650 independent reflections
1865 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.045$
$\theta_{\max} = 26.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.069$
$S = 0.91$
2650 reflections
172 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.036P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

C1—C11	1.429 (3)	C12—C13	1.440 (3)
C11—C12	1.192 (3)		
C5—C1—C2	107.25 (18)	C12—C11—C1	178.5 (3)
C5—C1—C11	126.0 (2)	C11—C12—C13	179.0 (2)
C11—C1—C2—C3	179.9 (2)	C12—C13—C14—C15	−179.1 (2)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

*Cg*1, *Cg*2 and *Cg*3 are the centroids of the C1–C5, C6–C10 and C13–C18 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7···*Cg*3$^{\rm ii}$	0.93	3.13	3.927 (3)	145
C14—H14···*Cg*2$^{\rm i}$	0.93	3.14	3.817 (3)	131
C15—H15···*Cg*2$^{\rm i}$	0.93	3.25	3.870 (3)	126
C18—H18···*Cg*1$^{\rm iii}$	0.93	2.72	3.535 (3)	147

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

All H atoms were refined using the riding-model approximation, with C—H = 0.93 Å for aromatic H atoms [$U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$] and C—H = 0.96 Å for methyl H atoms [$U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$].

For both compounds, data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3011). Services for accessing these data are described at the back of the journal.

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