(Z)-1-Ferrocenyl-3-(3-hydroxyanilino)-but-2-en-1-one and (Z)-1-ferrocenyl-3-(4-hydroxyanilino)but-2-en-1-one

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The title compounds, both $[Fe(C_5H_5)(C_{15}H_{14}NO_2)]$, crystallize with $Z' = 2$ in the centrosymmetric space group $P\bar{1}$. In each compound, there is an intramolecular $N-H\cdots O=C$ hydrogen bond, and pairs of intermolecular $O-H\cdots O=C$ hydrogen bonds link the molecules into chains, parallel to $[1\bar{1}0]$ in the 3-hydroxy compound and parallel to $[10\bar{1}]$ in the 4-hydroxy compound.

Comment

It has been shown (Shi, Yang, Shen et al., 2004; Shi, Yang, Song & Liu, 2004) that primary amines, Ar'NH$_2$, react smoothly with β-diketones, ArCOCH$_2$COR, to give enaminones, ArCOCH=C(NHAr')R, in good yields. In continuation of our investigation of the chemistry of ferrocenyl enaminones (Shi et al., 2005), we have synthesized the title compounds, viz. (C$_5$H$_5$)FeC$_5$H$_4$COCH=C(NHAr')CH$_3$, where Ar' is 3-HO-C$_6$H$_4$, (I), and 4-HOC$_6$H$_4$, (II). We report here the molecular and supramolecular structures of these isomeric organometallic compounds.
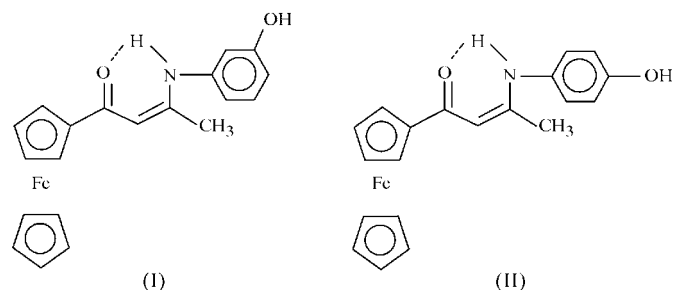
The title compounds crystallize with $Z' = 2$ in the space group $P\bar{1}$. In the two independent molecules, the bond lengths (Tables 1 and 3) are almost identical. As noted in the compounds previously reported, the $O=C-C=C-N$ unit is planar and the bond lengths indicate electron delocalization (Gilli et al., 2000; Shi, Yang, Shen et al., 2004; Shi, Yang, Song & Liu, 2004). However, for each of compounds (I) and (II),

the two distinct molecules show different conformations. The $O=C-C=C-N$ plane is twisted with respect to the benzene and substituted cyclopentadienyl rings by 70.5 (2) and 21.0 (3)° for (Ia), 66.4 (2) and 19.5 (3)° for (Ib), 53.56 (15) and 26.07 (17)° for (IIa), and 57.24 (15) and 24.95 (18)° for (IIb). Consistent with the large dihedral angles between the $O=C-C=C-N$ plane and the substituted cyclopentadienyl ring, the C10—C11 and C30—C31 bonds linking the $O=C-C=C-N$ group and the substituted cyclopentadienyl ring are typical of a single bond (Csp^2—Csp^2), suggesting that the substituted cyclopentadienyl ring is not involved in the conjugation of the $O=C-C=C-N$ group.

Although both compounds in the solid state have strong intramolecular $N-H\cdots O=C$ hydrogen bonds (Tables 2 and 4), their packing modes are markedly different. For compound (I), atom O2 in the type 1 molecule (Fig. 1a) at (x, y, z) acts as a hydrogen-bond donor to carbonyl atom O3 in the type 2 molecule at $(x - 1, 1 + y, z)$, so generating two infinite one-dimensional chains in the $[1\bar{1}0]$ direction, which are linked by an $O-H\cdots O=C$ hydrogen bond, viz. atom O4 in the type 2 molecule (Fig. 1b) at (x, y, z) acts as a donor to the type 1 atom O1 in the same asymmetric unit (Fig. 2). For compound (II), atom O2 in the type 1 molecule (Fig. 3a) at (x, y, z) acts as a hydrogen-bond donor to carbonyl atom O3 in the type 2 molecule at $(1 + x, y, z - 1)$, thus resulting in two $[10\bar{1}]$ infinite one-dimensional chains which are linked by an $O-H\cdots O=C$ hydrogen bond from atom O4 in the type 2 molecule (Fig. 3b) at (x, y, z) and the type 1 atom O1 in the same asymmetric unit (Fig. 4).

In addition to the above strong hydrogen bonds, weak $C-H\cdots\pi$(arene) hydrogen bonds are present in compounds (I)
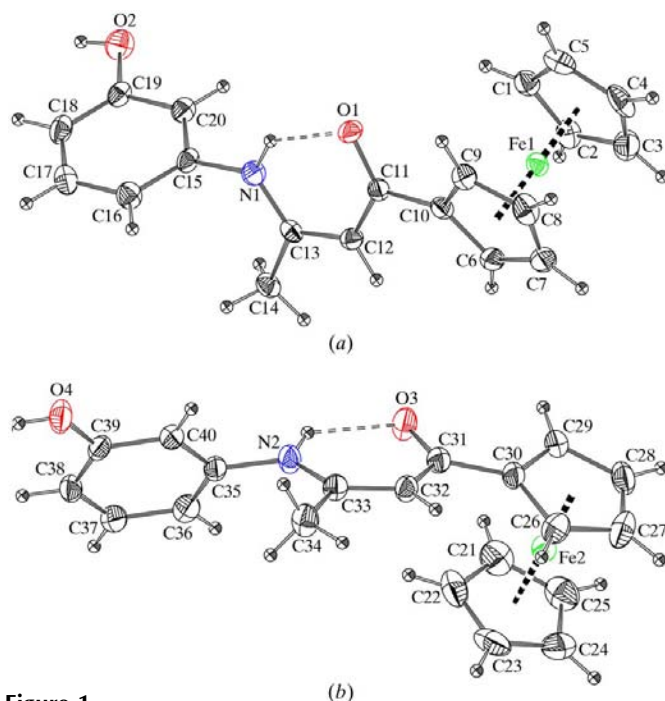

Figure 1
The two independent molecules of (I), showing the atom-labelling schemes for (a) molecule 1 and (b) molecule 2. Displacement ellipsoids are drawn at the 30% probability level.

metal-organic compounds

and (II) (Tables 2 and 4). For compound (I), atom C2 in the type 1 molecule at (x, y, z) acts as a hydrogen-bond donor to the C15–C20 ring in the type 1 molecule at $(-x, 2 - y, 1 - z)$, whereas atom C4 in the type 1 molecule at (x, y, z) acts as a donor to the C35–C40 ring in the type 2 molecule at $(1 - x,$
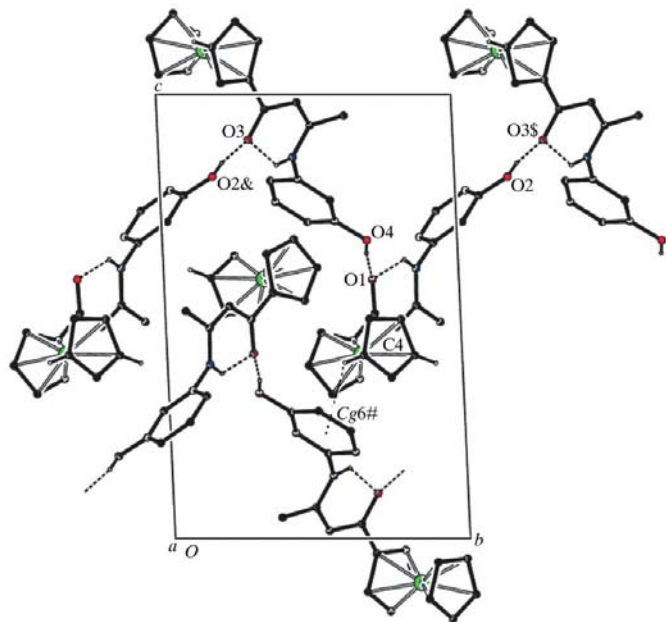

Figure 2
Part of the crystal structure of (I), showing the formation of the $[1\bar{1}0]$ chain linked by O—H···O≡C hydrogen bonds. For clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an ampersand (&) and a dollar sign ($) are at the symmetry positions $(1 + x, y - 1, z)$ and $(x - 1, 1 + y, z)$, respectively; $Cg6\#$ is at the symmetry position $(1 - x, 1 - y, 1 - z)$.
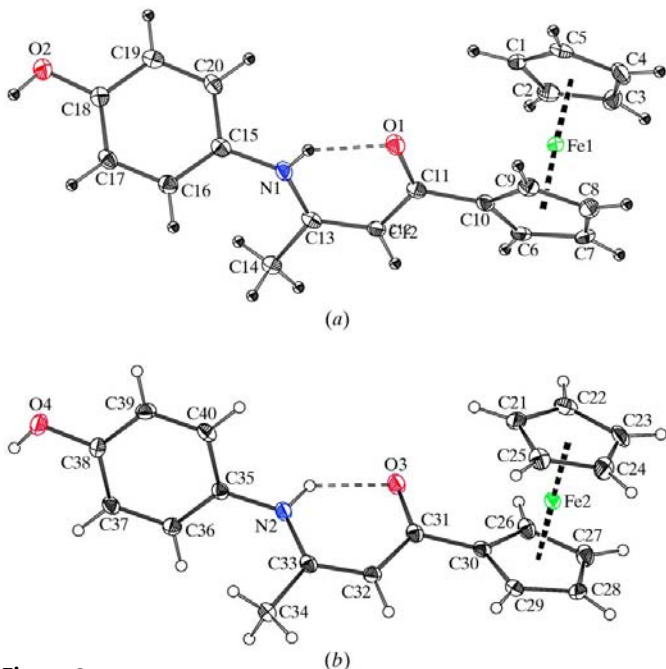

Figure 3
The two independent molecules of (II), showing the atom-labelling schemes for (a) molecule 1 and (b) molecule 2. Displacement ellipsoids are drawn at the 30% probability level.
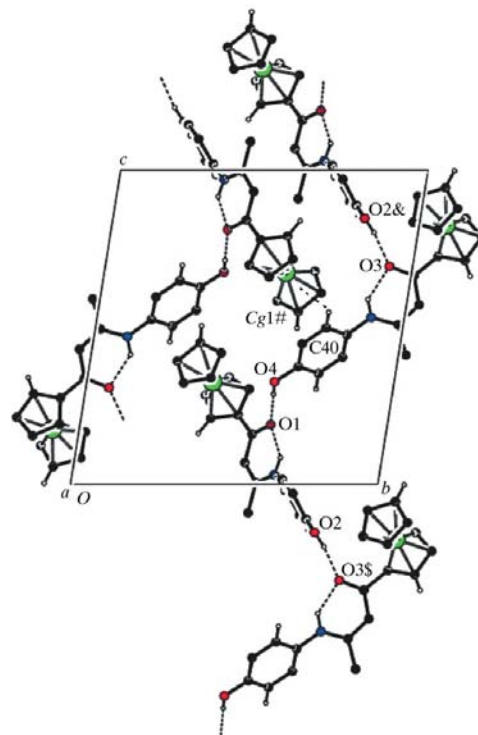

Figure 4
Part of the crystal structure of (II), showing the formation of the $[10\bar{1}]$ chain linked by O—H···O≡C hydrogen bonds. For clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an ampersand (&) and a dollar sign ($) are at the symmetry positions $(x - 1, y, 1 + z)$ and $(1 + x, y, z - 1)$, respectively; $Cg1\#$ is at the symmetry position $(1 - x, 1 - y, 1 - z)$.

$1 - y, 1 - z)$ (Fig. 2). Atom C28 in the type 2 molecule at (x, y, z) acts as a hydrogen-bond donor to the C15–C20 ring in the type 1 molecule at $(1 - x, 1 - y, 2 - z)$. For compound (II), atoms C4 and C6 in the type 1 molecule at (x, y, z) act as hydrogen-bond donors to the C35–C40 ring in the type 2 molecule at $(-x, 1 - y, 1 - z)$ and to the C15–C20 ring in the type 1 molecule at $(1 - x, 1 - y, -z)$, respectively. Atoms C23 and C29 in the type 2 molecule at (x, y, z) act as donors to the C15–C20 ring in the type 1 molecule at $(1 - x, 2 - y, 1 - z)$ and to the C35–C40 ring in the type 2 molecule at $(1 - x, 2 - y, 1 - z)$, respectively. Unlike compound (I), hydrogen bonds involving the cyclopentadienyl rings as acceptors are also observed; benzene atoms C37 and C40 in the type 2 molecule at (x, y, z) act as hydrogen-bond donors to the C26–C30 ring in the type 2 molecule at $(-x, 2 - y, 1 - z)$ and to the C1–C5 ring in the type 1 molecule at $(1 - x, 1 - y, 1 - z)$, respectively (Fig. 4).

Experimental

For the synthesis of each of compounds (I) and (II), a solution of ferrocenoylacetone (5 mmol) and the appropriate aminophenol (5 mmol) in anhydrous ethanol (20 ml) was stirred and refluxed for 20 h. After removal of the solvent, the resulting solids were purified by chromatography on silica gel, with ethyl acetate and dichloromethane [(I): 1:20 v/v; (II): 1:8 v/v] as eluant. Compounds (I) and (II) were recrystallized from dichloromethane/petroleum ether solutions to give red crystals in each case suitable for single-crystal X-ray

diffraction [(I): m.p. 480–481 K, yield 63%; (II): m.p. 490–492 K, yield 67%]. For (I), IR (KBr): 3424 (*m*, OH), 3076 (*m*, NH), 1588 (*vs*, O=C), 1523 (*m*, C=C) cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$): δ 12.502 (1H, *s*, NH), 9.019 (1H, *s*, OH), 7.139–7.165, 6.727–6.741, 6.673, 6.590–6.602 (4H, *t*, *d*, *s*, *d*, C$_6$H$_4$), 5.409 (1H, *s*, CH), 4.762, 4.397 (2H, 2H, 2*m*, C$_5$H$_4$), 4.141 (5H, *s*, C$_5$H$_5$), 2.020 (3H, *s*, CH$_3$). For (II), IR (KBr): 3426 (*m*, OH), 3090 (*m*, NH), 1585 (*vs*, O=C), 1510 (*vs*, C=C) cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$): δ 12.367 (1H, *s*, NH), 6.906–6.919, 6.775–6.788 (2H, *d*, 2H, *d*, C$_6$H$_4$), 5.373 (1H, *s*, CH), 4.720, 4.345 (2H, 2H, 2*m*, C$_5$H$_4$), 4.142 (6H, *s*, C$_5$H$_5$, OH), 1.955 (3H, *s*, CH$_3$).

Compound (I)

Crystal data

[Fe(C$_5$H$_5$)(C$_{15}$H$_{14}$NO$_2$)]
$M_r = 361.21$
Triclinic, $P\bar{1}$
$a = 9.768$ (2) Å
$b = 10.804$ (2) Å
$c = 16.244$ (3) Å
$\alpha = 91.39$ (3)°
$\beta = 97.05$ (3)°
$\gamma = 99.22$ (3)°

$V = 1677.7$ (6) Å^3
$Z = 4$
$D_x = 1.430$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.91$ mm^{-1}
$T = 293$ K
Block, red
$0.30 \times 0.20 \times 0.20$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scan
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.772$, $T_{max} = 0.839$
6988 measured reflections

6576 independent reflections
3837 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 26.0°$
3 standard reflections
　every 200 reflections
　intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.126$
$S = 1.01$
6576 reflections
437 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 0.8184P]$
　where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Table 1
Selected bond lengths (Å) for (I).

O1—C11	1.265 (5)	O3—C31	1.256 (5)
N1—C13	1.340 (5)	N2—C33	1.348 (5)
N1—C15	1.429 (5)	N2—C35	1.423 (5)
C10—C11	1.491 (6)	C30—C31	1.470 (6)
C11—C12	1.400 (6)	C31—C32	1.417 (6)
C12—C13	1.376 (6)	C32—C33	1.369 (6)
C13—C14	1.493 (5)	C33—C34	1.503 (6)

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

$Cg3$ and $Cg6$ are the centroids of the C15–C20 and C35–C40 rings, respectively.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1N$\cdots$O1	0.86	1.96	2.642 (5)	136
N2—H2N$\cdots$O3	0.86	1.99	2.645 (5)	132
O2—H2O$\cdots$O3^i	0.82	1.82	2.629 (5)	170
O4—H4O$\cdots$O1	0.82	1.86	2.679 (5)	172
C2—H2$\cdots Cg3^{ii}$	0.93	2.85	3.686 (5)	150
C4—H4$\cdots Cg6^{iii}$	0.93	2.89	3.614 (5)	135
C28—H28$\cdots Cg3^{iv}$	0.93	2.96	3.655 (6)	133

Symmetry codes: (i) $x - 1, y + 1, z$; (ii) $-x, -y + 2, -z + 1$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $-x + 1, -y + 1, -z + 2$.

Compound (II)

Crystal data

[Fe(C$_5$H$_5$)(C$_{15}$H$_{14}$NO$_2$)]
$M_r = 361.21$
Triclinic, $P\bar{1}$
$a = 7.4100$ (11) Å
$b = 14.687$ (2) Å
$c = 15.5601$ (19) Å
$\alpha = 80.370$ (7)°
$\beta = 77.677$ (7)°
$\gamma = 86.297$ (8)°

$V = 1630.3$ (4) Å^3
$Z = 4$
$D_x = 1.472$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.94$ mm^{-1}
$T = 173$ K
Block, red
$0.30 \times 0.15 \times 0.12$ mm

Data collection

Rigaku Mercury diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{min} = 0.767$, $T_{max} = 0.896$

15645 measured reflections
5891 independent reflections
4742 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 25.4°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.105$
$S = 1.10$
5891 reflections
438 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 1.0012P]$
　where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}

Table 3
Selected bond lengths (Å) for (II).

O1—C11	1.269 (4)	O3—C31	1.275 (4)
N1—C13	1.336 (4)	N2—C33	1.337 (4)
N1—C15	1.427 (4)	N2—C35	1.423 (4)
C10—C11	1.482 (4)	C30—C31	1.481 (4)
C11—C12	1.406 (4)	C31—C32	1.413 (4)
C12—C13	1.391 (4)	C32—C33	1.386 (4)
C13—C14	1.498 (4)	C33—C34	1.502 (4)

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

$Cg1$, $Cg3$, $Cg5$ and $Cg6$ are the centroids of the C1–C5, C15–C20, C26–C30 and C35–C40 rings, respectively.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1N$\cdots$O1	0.88	1.89	2.607 (3)	138
N2—H2N$\cdots$O3	0.88	1.91	2.623 (3)	137
O2—H2O$\cdots$O3^i	0.84	1.80	2.632 (3)	170
O4—H4O$\cdots$O1	0.84	1.82	2.651 (3)	169
C4—H4$\cdots Cg6^{ii}$	0.95	2.94	3.696 (4)	137
C6—H6$\cdots Cg3^{iii}$	0.95	2.76	3.673 (3)	161
C23—H23$\cdots Cg3^{iv}$	0.95	2.84	3.592 (4)	137
C29—H29$\cdots Cg6^{iv}$	0.95	2.92	3.786 (4)	152
C37—H37$\cdots Cg5^{v}$	0.95	2.97	3.710 (3)	135
C40—H40$\cdots Cg1^{vi}$	0.95	2.93	3.663 (3)	135

Symmetry codes: (i) $x + 1, y, z - 1$; (ii) $-x, -y + 1, -z + 1$; (iii) $-x + 1, -y + 1, -z$; (iv) $-x + 1, -y + 2, -z + 1$; (v) $-x, -y + 2, -z + 1$; (vi) $-x + 1, -y + 1, -z + 1$.

All H atoms in (I) and (II) were placed at geometrically idealized positions and subsequently treated as riding atoms [C—H = 0.93 (aromatic and olefinic) and 0.96 Å (CH$_3$), N—H = 0.86 Å and O—H = 0.82 Å at 293 K for (I), and C—H = 0.95 (aromatic and olefinic) and 0.98 Å (CH$_3$), N—H = 0.88 Å and O—H = 0.84 Å at 173 K for (II)]. U_{iso}(H) values were set at $1.2U_{eq}$(C,N) or $1.5U_{eq}$(C$_{methyl}$,O).

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989) for (I) and *CrystalClear* (Rigaku, 2001) for (II); cell

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3037). Services for accessing these data are described at the back of the journal.

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