Methyl 2-(4-ferrocenylbenzamido)-thiophene-3-carboxylate and ethyl 2-(4-ferrocenylbenzamido)-1,3-thiazole-4-acetate, a unique ferrocene derivative containing a thiazole moiety

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The conformations and hydrogen bonding in the thiophene and thiazole title compounds, $[Fe(C_5H_5)(C_{20}H_{14}NO_3S)]$, (I), and $[Fe(C_5H_5)(C_{19}H_{17}N_2O_3S)]$, (II), are discussed. The sequence $(C_5H_4)–(C_6H_4)–(CONH)–(C_4H_2S)–(CO_2Me)$ of rings and moieties in (I) is close to being planar; all consecutive interplanar angles are less than 10°. An intramolecular $N–H\cdots O=C_{ester}$ hydrogen bond [graph set $S(6)$, $N\cdots O = 2.768 (2)$ Å and $N–H\cdots O = 134 (2)°$] effects the molecular planarity, and aggregation occurs via hydrogen-bonded chains formed from intermolecular $C_{ar}–H\cdots O=C_{ester/amide}$ interactions along [010], with $C\cdots O$ distances ranging from 3.401 (3) to 3.577 (2) Å. The thiazole system in (II) crystallizes with two molecules in the asymmetric unit; these differ in the conformation along their long molecular axes; for example, the interplanar angle between the phenylene (C_6H_4) and thiazole (C_3NS) rings is 8.1 (2)° in one molecule and 27.66 (14)° in the other. Intermolecular $N–H\cdots O=C_{ester}$ hydrogen bonds [$N\cdots O = 2.972 (4)$ and 2.971 (3) Å], each augmented by a $C_{phenylene}–$

$H\cdots O=C_{ester}$ interaction [3.184 (5) and 3.395 (4) Å], form motifs with graph set $R_2^1(7)$ and generate chains along [100]. The amide $C=O$ groups do not participate in hydrogen bonding. Compound (II) is the first reported ferrocenyl-containing thiazole structure.

Comment

Ferrocene (Fc) and its derivatives continue to attract much attention in coordination chemistry, with important roles encompassing both structural and electronic capabilities (Adams, 1999). Integration of ferrocene into new hybrid systems has expanded the potential of organometallic materials with a range of feasible applications (Togni & Halterman, 1998; Togni & Hayashi, 1995; Hudson et al., 2001). We report here the structures of two 4-ferrocenylbenzamide systems with terminal thiophenecarboxylate, (I), and thiazoleacetate groups, (II).
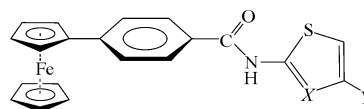
(I) X=C–CO₂Me; Y=H
(II) X=N; Y=CH₂CO₂Et

A view of (I) with the atomic numbering scheme is shown in Fig. 1. Bond lengths and angles are in accord with anticipated values (Allen, 2002). In (I), the Fe—C bond lengths for the substituted η^5-C_5H_4 ring are in the range 2.038 (2)–2.054 (2) Å and are similar to those in the η^5-C_5H_5 ring [2.037 (2)–2.054 (2) Å]; the $Fe\cdots Cg1$ and $Fe\cdots Cg2$ distances are 1.6462 (10) and 1.6525 (10) Å, respectively, the $Cg1\cdots Fe1\cdots Cg2$ angle is 177.20 (5)°, and the C_5/C_5 interplanar angle is 3.81 (15)° [$Cg1$ and $Cg2$ are the η^5-C_5H_4 and η^5(C_5H_5) ring centroids, respectively]. The $\eta^5 C_5$ rings are slightly staggered from eclipsed geometry, with the five $C1n\cdots Cg1\cdots Cg2\cdots C2n$ pseudo-torsion angles in the range 12.24 (16)–12.79 (15)° ($n = 1$–5).

The related 4-$FcC_6H_4CO_2R$ carboxylates [R = Me (Savage et al., 2002), Et and ^iPr (Anderson et al., 2003)] have conformations that can be defined by the interplanar angles between the η^5-C_5H_4 and C_6H_4 rings, and between the C_6H_4 ring and carboxylate CO_2R group. These are, respectively, 9.35 (13) and 8.5 (2)° for Me, 6.88 (12) and 2.59 (17)° for Et, and 10.5 (2) and 19.5 (5)° for ^iPr. In (I), the $(C_5H_4)–(C_6H_4)–(CONH)–(C_4H_2S)–(CO_2Me)$ system has interplanar angles between successive C_5H_4, C_6H_4, CONH, C_4H_2S and CO_2Me moieties of
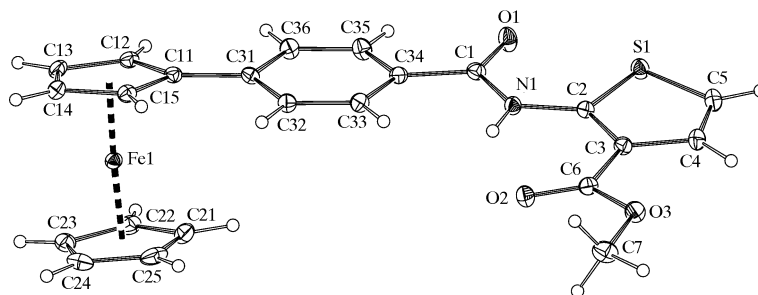
Figure 1
A view of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

9.36 (11), 8.79 (17), 1.97 (14) and 6.33 (11)°, respectively. Apart from slight twisting, no ring bending occurs along the long molecular axis as a result of steric effects; this situation is in contrast to that found in 2-(ferrocenyl)thiophene-3-carboxylic acid (Gallagher *et al.*, 2001), where significant bending from linearity occurs in the thienyl ring relative to the η^5-C_5H_4 ring to which it is bonded.

Methyl 2-[(ferrocenylcarbonyl)amino]thiophene-3-carboxylate, $(C_5H_5)Fe(C_5H_4)$–(CONH)–(C_4H_2S)–(CO_2Me), (III) (Alley *et al.*, 2005), differs from (I) in that it does not have the 1,4-phenylene C_6H_4 ring between the C_5H_4 and CONH groups. Geometric data are comparable in the two structures, with maximum differences within 0.01 Å and 2° for the amidothiophenecarboxylate residues. The C—S—C and S—C—N(H) angles are 90.98 (10) and 123.58 (15)° in (I), and 90.93 (11) and 123.54 (16)° in (III); the Cambridge Structural Database (CSD; Version 5.26 of February 2005; Allen, 2002) average for thiophene C—S—C angles is 92.0° (range 88.7–97.9°). For S—C═$C_{carboxy}$ angles, the average is 111.4° (range 105.5–113.9°); the equivalent S1—C2═C3 angles in (I) and (III) are 111.89 (15) and 111.94 (15)°, respectively (Allen, 2002). CSD analysis shows that both (I) and (III) have regular amidothiophenecarboxylate moieties.

An intramolecular N—H···O═C_{ester} hydrogen bond (Table 1) forms a ring in (I), with graph set $S(6)$ (Bernstein *et al.*, 1995), thus enforcing planarity along the molecular axis; the N···O distance is 2.768 (2) Å, slightly longer than the corresponding value [2.727 (2) Å] in (III). Molecules of (I) assemble as one-dimensional chains along the *b*-axis direction through C—H···O═C interactions, as shown in Fig. 2 with details in Table 1. These generate $R_2^1(7)$ and $R_3^2(15)$ motifs that, in combination with the $S(6)$ ring, produce a larger $R_2^2(20)$ ring. Overall, the crystal structure comprises one-dimensional chains, aggregating *via* weak C7—H7C···π(thienyl)^{iii} contacts (H7C···Cg3^{iii} = 2.83 Å; symmetry code as in Table 1), which link pairs of screw-axis-related chains to form a ladder extending along [010]; there are normal van der Waals separations between pairs of ladders. Examination of (I) with *PLATON* (Spek, 2002) reveals no solvent-accessible voids in the crystal structure and a packing index of 72.6.

Compound (II) is the first structurally characterized ferrocene derivative containing a thiazole moiety to be reported, and this compound crystallizes with two molecules (*A* and *B*) in the asymmetric unit of space group $P\bar{1}$, as shown in Figs. 3(*a*) and 3(*b*). The conformations of these molecules differ slightly along their long molecular axes with respect to the orientations of the amidothiazoleacetate groups, and there is some minor ethoxy disorder [0.915 (7):0.085 (7)] in molecule *A*. Bond lengths and angles are unexceptional and are comparable to data available from corresponding fragments available in the CSD.

In (II), the Fe—C bond lengths for the η^5-C_5H_4 ring in *A* are in the range 2.031 (4)–2.048 (3) Å and are similar to those [2.033 (3)–2.040 (4) Å] for the η^5-C_5H_5 ring. Molecule *B* has similar values [2.032 (4)–2.047 (3) Å] for the substituted ring but two contrasting Fe···η^5-C_5H_5 bond lengths [*i.e.* Fe1—

C23*B*/C24*B* = 2.005 (4)/2.023 (5) Å]. These Fe—C C atoms have the largest U_{eq} values, *cf.* 0.0785 (17) and 0.0733 (15) Å^2 *versus* an average U_{eq} of 0.043 Å^2 for all 48 C atoms present (Spek, 2002); however, no disorder is present and the bond-length contraction must be a result of a small measure of librational motion and ring slippage (0.06 Å). The Fe···Cg1/Cg2 distances are 1.6407 (17) and 1.6450 (18) Å in *A*, and 1.6400 (17) and 1.644 (2) Å in *B*, the Cg1···Fe1···Cg2 angles are 178.76 (9) and 178.96 (10)°, and both C_5/C_5 interplanar angles are 1.6 (3)° [Cg1 and Cg2 are defined as for (I) above]. The $\eta^5 C_5$ rings deviate from eclipsed geometry, with five C1*n*···Cg1···Cg2···C2*n* (*n* = 1–5) pseudo-torsion angles ranging from 13.5 (3) to 14.5 (3)° in *A* and from 5.7 (3) to 7.3 (3)° in *B*, in the same sense as in *A*.

A minor conformational difference between molecules *A* and *B* is in the orientation of the Fc—C_6H_4– moiety with respect to the CONH–(thiazolyl)–CO_2Et fragment, resulting in the O1*A*—C1*A*—C34*A*—C33*A* [171.9 (3)°] and O1*B*—C1*B*—C34*B*—C33*B* [161.3 (3)°] torsion angles being significantly different. The amidothiazole groups adopt similar conformations in the two molecules, with N—H *cis* to N and C═O *cis* to S. A search of the CSD for this fragment gave 11 hits all with this same orientation, indicating that this is a preferred solid-state conformation. The *cis*-oriented pairs of N···N and O···S distances are 2.333 (4) and 2.342 (4) Å, and 2.669 (2) and 2.660 (3) Å, respectively, and are oriented in a suitable fashion for bidentate coordination to metal systems. As found for (I), molecule *A* contains consecutive ring and moiety planes that are essentially coplanar along the long molecular axis; however, in molecule *B*, the interplanar twists are larger; for example, the C_6H_4 and amide O═C—N(H)
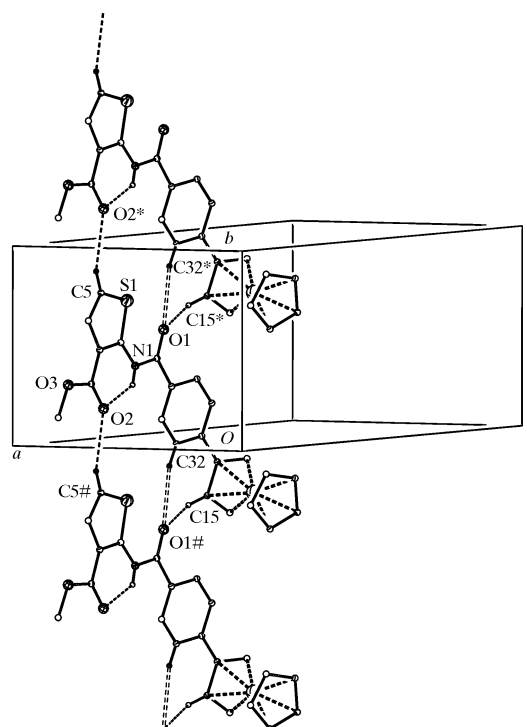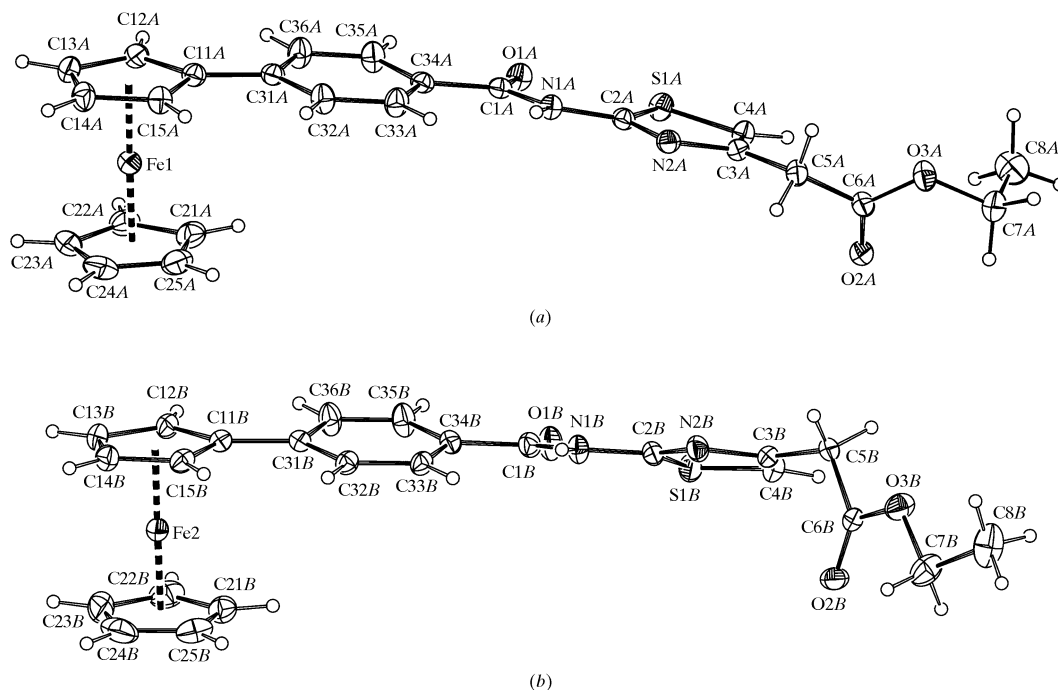

Figure 2
A view of the hydrogen-bond interactions (dashed lines) in the crystal structure of (I). [Symmetry codes: (*) *x*, 1 + *y*, *z*; (#) *x*, −1 + *y*, *z*.]
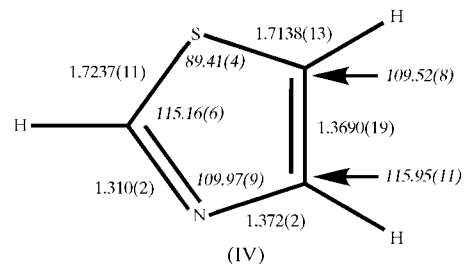
Figure 3
(a) A view of the major conformer of molecule A in (II) and (b) a view of molecule B in (II), with the atomic numbering schemes. Displacement ellipsoids are drawn at the 30% probability level.

group planes are inclined at an angle of 17.2 (3)° (Figs. 3a and 3b). In tandem, slight bending occurs along the long molecular axis in molecule A, as evidenced by the C11n—C31n⋯C34n angle [176.4 (2)°; $n = A$ or B], in contrast to the near linear value [178.46 (19)°] in B.

In (II), intermolecular N_{amide}—H⋯O=C_{ester} hydrogen bonds link the molecules, forming chains extending along [100], as shown in Fig. 4 with details in Table 2. This inter-action, in combination with C—H⋯O=C_{ester} interactions, results in hydrogen-bonded rings with graph set $R_2^1(7)$, augmented by weaker secondary contacts C7B*⋯N2A and C7A⋯N2B (involving thiazole N atoms). Combination with the N—H⋯O=C hydrogen bonds produces rings with graph sets $R_2^2(9)$ and, overall for the pairs of rings, $R_2^2(12)$. The chains are linked into a ladder structure extending along [100] by C5A—H5A⋯π(thiaz-B)# interactions [symmetry code: (#) $-x, -y, 1 - z$; C5A⋯π(thiaz-centroid) = 3.511 (4) Å]. No comparable C5B⋯π(thiaz-A) interaction is present; the thiazole S atoms and amide C=O groups are not involved in

hydrogen bonding. The packing index is 68.9 based on the major conformation of molecule A.

Of interest for comparison with (II) are the high-precision structural data for the molecular structure of thiazole (IV) from a combined analysis of gas-phase electron diffraction data, rotational constants and *ab initio* calculations (Bone *et al.*, 1999). The corresponding mean values for (II) are S—C(C) = 1.713 (2) Å, S—C(N) = 1.730 (6) Å, C—N = 1.391 (2) Å and C=N = 1.299 (2) Å, demonstrating that the thiazole groups are relatively unperturbed through molecular or crystal packing forces in (II) and are comparable to the gas-phase structure data for (IV).

(IV)

A search for amidothienyl and amidothiazolyl fragments in crystal structures in the CSD reveals seven and 21 systems (with coordinates), respectively. A search for structures incorporating the ferrocenyl moiety (as C_5FeC_5) and a thio-phene-type heteroaromatic ring yielded 30 structures; when the thiophene-type ring was replaced with a thiazole hetero-aromatic ring, there were no hits. This lack of structural data is somewhat unusual given the vast output of structural ferro-cene research to date (Adams, 1999; Allen 2002). For comparison, a CSD search with ferrocene and pyridinyl (as C_5N) gives a total of 335 structures, revealing the wealth of structural data available for N-heteroaromatic groups, such as

Figure 4
The hydrogen-bonding pattern involving molecules A and B in (II). Hydrogen bonds are shown as dashed lines. [Symmetry codes: (*) $1 - x, 1 - y, 1 - z$; ($) $-x, 1 - y, 1 - z$.]

pyridine donor ligands, in ferrocene chemistry when compared with S-heteroaromatic systems, such as thiazole (Allen, 2002). Studies are in progress to extend the synthetic, structural and electrochemistry of these new systems in coordination chemistry.

Experimental

Compounds (I) and (II) were synthesized according to standard coupling procedures using 4-ferrocenylbenzoic acid as its acid chloride and methyl 2-aminothiophene-3-carboxylate or ethyl 2-amino-4-thiazoleacetate in yields of *ca* 30 and 26%, respectively. Recrystallization, in both cases, was undertaken from petroleum spirits/Et$_2$O to produce red plates, (I) (m.p. 487–489 K), and an orange crystalline solid, (II) (421–423 K). Crystals suitable for X-ray diffraction studies were grown by diffusion of pentane vapour into a CH$_2$Cl$_2$ solution of the appropriate compound. Although the syntheses are uncomplicated, problems arose during the purification of (I) as it decomposes on both silica and alumina to give the starting materials plus a third compound, identified by ^{1}H and ^{13}C NMR as methyl 4-ferrocenylbenzoate. Isolation of modest quantities of (I) was achieved by repeated recrystallization of column fractions, though the eventual overall yield was poor.

Compound (I)

Crystal data

[Fe(C$_5$H$_5$)(C$_{20}$H$_{14}$NO$_3$S)]
$M_r = 445.30$
Monoclinic, $P2_1/n$
$a = 10.1428$ (3) Å
$b = 8.0965$ (2) Å
$c = 23.0557$ (7) Å
$\beta = 95.4912$ (14)°
$V = 1884.67$ (9) Å^3
$Z = 4$

$D_x = 1.569$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6335 reflections
$\theta = 2.6$–27.5°
$\mu = 0.94$ mm^{-1}
$T = 150$ (1) K
Plate, red
$0.22 \times 0.16 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer
φ scan and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.820$, $T_{max} = 0.912$
6335 measured reflections

4313 independent reflections
3441 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 27.5$°
$h = -13 \rightarrow 13$
$k = -10 \rightarrow 10$
$l = -25 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.088$
$S = 1.06$
4313 reflections
268 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 1.226P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.63$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0024 (6)

Table 1
Hydrogen-bond geometry (Å, °) for (I).

$Cg3$ is the centroid of the thiophene ring.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2	0.81 (2)	2.14 (2)	2.768 (2)	134 (2)
C5—H5···O2^i	0.95	2.56	3.411 (3)	150
C15—H15···O1^{ii}	0.95	2.56	3.401 (3)	147
C32—H32···O1^{ii}	0.95	2.65	3.577 (2)	165
C7—H7C···$Cg3^{iii}$	0.98	2.83	3.604 (2)	136

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

Compound (II)

Crystal data

[Fe(C$_5$H$_5$)(C$_{19}$H$_{17}$NO$_3$S)]
$M_r = 474.36$
Triclinic, $P\bar{1}$
$a = 12.7466$ (4) Å
$b = 12.8752$ (8) Å
$c = 13.5661$ (7) Å
$\alpha = 91.811$ (3)°
$\beta = 106.096$ (3)°
$\gamma = 92.735$ (3)°
$V = 2134.35$ (18) Å^3

$Z = 4$
$D_x = 1.476$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12087 reflections
$\theta = 2.6$–27.5°
$\mu = 0.83$ mm^{-1}
$T = 150$ (1) K
Needle, red
$0.20 \times 0.07 \times 0.04$ mm

Data collection

Nonius KappaCCD diffractometer
φ scan and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.851$, $T_{max} = 0.967$
15129 measured reflections

9714 independent reflections
5617 reflections with $I > 2\sigma(I)$
$R_{int} = 0.069$
$\theta_{max} = 27.5$°
$h = -16 \rightarrow 16$
$k = -16 \rightarrow 16$
$l = -16 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.127$
$S = 1.00$
9714 reflections
573 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0472P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0015 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H1A···O2B^{iv}	0.88	2.12	2.972 (4)	162
N1B—H1B···O2A^{v}	0.88	2.18	2.971 (3)	149
C33A—H33A···O2B^{iv}	0.95	2.24	3.184 (5)	173
C33B—H33B···O2A^{v}	0.95	2.46	3.395 (4)	167
C7A—H72···N2B^{v}	0.99	2.68	3.654 (6)	168
C7B—H75···N2A^{iv}	0.99	2.56	3.536 (5)	169

Symmetry codes: (iv) $-x, -y + 1, -z + 1$; (v) $-x + 1, -y + 1, -z + 1$.

Compound (I) crystallized in the monoclinic system; space group $P2_1/n$ was assigned from the systematic absences and confirmed by the analysis. Compound (II) crystallized in the triclinic system; space group $P\bar{1}$ was assumed and confirmed by the analysis, and the asymmetric unit was chosen so as to show clearly the overall similarity of the two independent molecules A and B. It became obvious during the refinement of (II) that there was some slight disorder at the terminal O3A—C7A—C8A moiety and this was allowed for. In the final refinement cycles, the bond lengths of the disordered ester group of molecule A were restrained *via* soft DFIX restraints to be the same as in the ordered molecule B; a common isotropic displacement parameter of 0.035 Å^2 was assigned to the minor-occupancy atoms. The final refined occupancies for the major and minor conformers were 0.915 (7) and 0.085 (7). In (I) and (II) [except for atom H1 bonded to N1 in (I)], all H atoms bound to C and N atoms were treated as riding, with U_{iso}(H) values of $1.5U_{eq}$(C) for methyl H atoms and $1.2U_{eq}$(C,N) for the remainder (methyl C—H = 0.98 Å, methylene C—H = 0.99 Å, aromatic C—H = 0.95 Å and amide N—H = 0.88 Å). The N1—H1 distance in (I) refined to 0.81 (2) Å.

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski &

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1846). Services for accessing these data are described at the back of the journal.

References

Adams, R. D. (1999). *J. Organomet. Chem.* **619**, 1–875.

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Alley, S., Gallagher, J. F., Kenny, P. T. M. & Lough, A. J. (2005). *Acta Cryst.* E**61**, m201–m203.

Anderson, F. P., Gallagher, J. F., Kenny, P. T. M., Ryan, C. & Savage, D. (2003). *Acta Cryst.* C**59**, m13–m15.

Bernstein, J., Davies, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bone, S. F., Smart, B. A., Gierens, H., Morrison, C. A., Brain, P. T. & Rankin, D. W. H. (1999). *Phys. Chem. Chem. Phys.* **1**, 2421–2426.

Ferguson, G. (1998). *PREP8*. University of Guelph, Canada.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Gallagher, J. F., Hudson, R. D. A. & Manning, A. R. (2001). *Acta Cryst.* C**57**, 28–30.

Hudson, R. D. A., Asselsbergh, I., Clays, K., Cuffe, L. P., Gallagher, J. F., Manning, A. R., Persoons, A. & Wostyn, K. (2001). *J. Organomet. Chem.* **637**, 435–444.

McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.

Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Savage, D., Gallagher, J. F., Ida, Y. & Kenny, P. T. M. (2002). *Inorg. Chem. Commun.* **5**, 1034–1040.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2002). *PLATON*. University of Utrecht, The Netherlands.

Togni, A. & Halterman, R. L. (1998). Editors. *Metallocenes*. Weinheim, Germany: Wiley-VCH.

Togni, A. & Hayashi, T. (1995). Editors. *Ferrocenes: Homogeneous Catalysis – Organic Synthesis – Materials Science*. Weinheim, Germany: VCH.