metal-organic compounds

Intermolecular interactions in two (ferrocenylmethyl)benzimidazoles incorporating the 4-MeOC$_6$H$_4$ and 3,4-(MeO)$_2$C$_6$H$_3$ groups: analysis of MeO—C—C distortions from ideal 120° geometry

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The title compounds, 1-ferrocenylmethyl-2-(4-methoxyphenyl)-1*H*-benzimidazole, [Fe(C$_5$H$_5$)(C$_{20}$H$_{17}$N$_2$O)], (I), and 2-(3,4-dimethoxyphenyl)-1-ferrocenylmethyl-1*H*-benzimidazole, [Fe(C$_5$H$_5$)(C$_{21}$H$_{19}$N$_2$O$_2$)], (II), are model electroactive compounds for anion sensor and antimalarial applications. Distortions from the ideal 120° angle about the MeO—C—C groups are evident, with angles of 115.1 (2) and 125.0 (2)° in (I), and 115.9 (2) and 124.6 (2)°, and 115.7 (2) and 125.1 (2)° in (II). The main intermolecular hydrogen bonds in (I) comprise C—H···N and C—H···π(C$_5$H$_5$) interactions, while in (II), only weak C—H···π(imidazole) and C—H···π(arene) interactions are present.

Comment

The synthesis of anion receptors is currently an area of intense research activity, due primarily to the ubiquitous roles which anions play in both chemical and biological processes, for example as substrates or co-factors for enzymes, and as nucleophiles, redox agents and phase-transfer catalysts. In the past decade, combinations of organometallic moieties with amide functionalities have been demonstrated to be essential components in many anion receptors (Beer, 1998; Kingston *et al.*, 1999). Recently, 1,3-disubstituted imidazolium cations have been utilized as such (Sato *et al.*, 1999; Thomas *et al.*, 2000), and their synthetic intermediates (imidazolin-2-ylidenes) are of interest as carbenes and are the subject of several synthetic and structural investigations (Benito *et al.*, 1995; Bildstein *et al.*, 1998, 1999; Li *et al.*, 1998).

Benzimidazole systems have attracted our attention in synthetic and applied biological research (Howarth *et al.*, 2000; Thomas *et al.*, 2000; Howarth & Hanlon, 2001; Gallagher, Hanlon *et al.*, 2001). Compounds (I) and (II), shown in Figs. 1

and 2, respectively, were obtained from the respective reactions of 2-(4-methoxyphenyl)- and 2-(3,4-dimethoxyphenyl)-benzimidazole with (ferrocenylmethyl)trimethylammonium iodide (Pauson *et al.*, 1966; Ferguson *et al.*, 1994) and K$_2$CO$_3$ in refluxing CH$_3$CN (details in *Experimental*). These compounds and close relatives are important electroactive model compounds for application in anion sensor studies (Thomas *et al.*, 2000), as well as in malarial parasite research (Howarth & Hanlon, 2001).
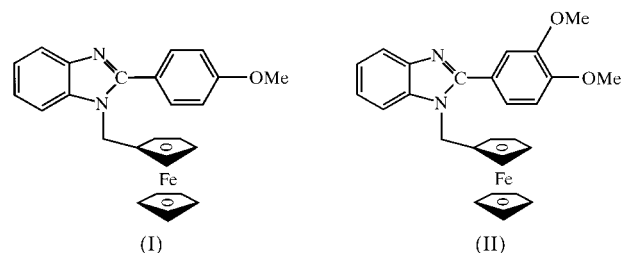
The Fe1—C bond lengths for the substituted cyclopentadienyl ring of (I) are in the range 2.036 (2)–2.0456 (18) Å and these are similar to the values of 2.033 (2)–2.039 (2) Å in the unsubstituted ring; for (II), these values are 2.030 (2)–2.049 (2) and 2.037 (2)–2.044 (2) Å, respectively. In (I), the cyclopentadienyl C—C bond-length ranges are small: 1.413 (3)–1.423 (3) and 1.399 (4)–1.413 (4) Å for the η^5(C$_5$H$_4$) and η^5(C$_5$H$_5$) rings, respectively; for (II), these values are 1.402 (4)–1.422 (3) and 1.393 (4)–1.410 (4) Å, respectively. In (I), the Fe1···Cg1 and Fe1···Cg2 distances are 1.6450 (9) and 1.6487 (12) Å, respectively, and Cg1···Fe1···Cg2 is 179.80 (7)°, where Cg1 and Cg2 are the centroids of the η^5(C$_5$H$_4$) and η^5(C$_5$H$_5$) rings, respectively; in (II), these values are, respectively, 1.6462 (11) and 1.6571 (12) Å, and 178.32 (6)°. The analogous data for ferrocenylmethyl(3-
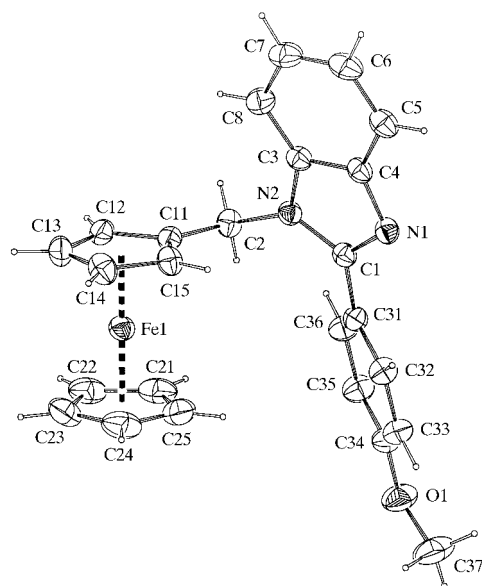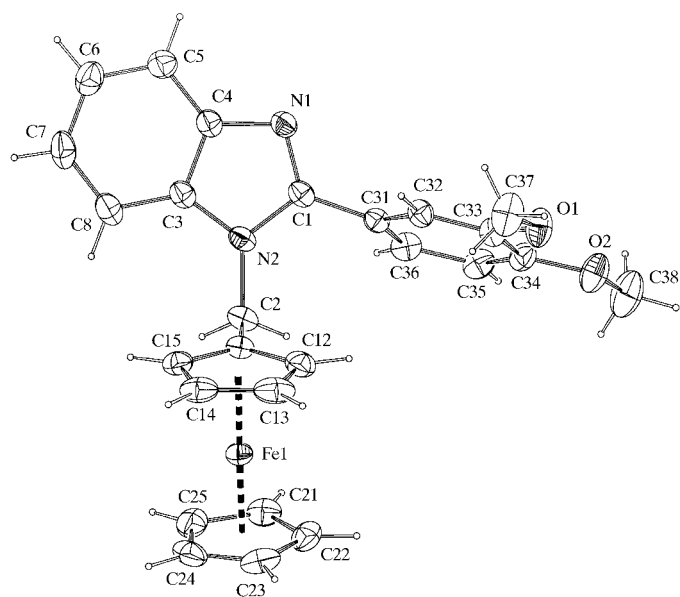

Figure 1
A view of the molecule of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

chlorophenyl)benzimidazole, (III) (Gallagher, Hanlon *et al.*, 2001), are 1.6467 (10) and 1.6487 (11) Å, and 179.12 (7)°, and for 2-(ferrocenyl)thiophene-3-carboxylic acid, (IV) (Gallagher, Hudson & Manning, 2001), 1.6435 (10) and 1.656 (3) Å, and 178.42 (11)°. These results highlight the similarity in the ferrocenyl bond lengths and angles in (I), (II) and (III). The cyclopentadienyl rings deviate from an eclipsed geometry in (I), as evidenced by the C1$n\cdots$Cg1$\cdots$Cg2$\cdots$C2n torsion angles [17.0 (2)–17.5 (2)°; n = 1–5], and in (II) [17.7 (2)–18.36 (18)°], which contrasts with the eclipsed geometry in (III) but is similar to the 20.6 (5)–21.3 (5)° range in the major conformation of (IV) (Gallagher, Hudson & Manning, 2001).

The molecular conformations adopted by (I) and (II) are different, with angles of 78.07 (8) and 40.22 (9)° between the C$_5$H$_4$/imidazolyl rings and the imidazolyl/phenyl rings, respectively, in (I), and 73.86 (8) and 70.02 (7)°, respectively, in (II); these angles are 84.37 (9) and 56.21 (8)°, respectively, in (III). An interesting difference between (I) and (II) arises about N2, with the C1—N2—C2/C3—N2—C2 angles differing by almost 7° in (I) but being similar in (II). A smaller variation at C1 of 2.5° is observed in (I). These differences arise due to the different molecular and packing geometries in (I) and (II), while the disparity in (III) is intermediate between (I) and (II). Differences are also evident in the Fe—C—C—N torsion angles (Tables 1 and 3).

Analysis of the hydrogen bonding in (I) reveals a (Cp)C13—H13$\cdots$N1[i] and a side-on C2—H2$B\cdots$N1[ii] intermolecular interaction, and two C—H$\cdots\pi$(C$_5$H$_5$) interactions (Fig. 3); details and symmetry codes are given in Table 2. The C2—H2$B\cdots$Cg3 descriptor (Cg3 is the imidazolyl ring centroid) gives H2$B\cdots$Cg3 2.86 Å, C2—H2$B\cdots$Cg3 135° and C2$\cdots$Cg3 3.605 (2) Å, stressing the acceptor as N and the interaction as C—H$\cdots$N not C—H$\cdots\pi$(imidazole). The C—

H$\cdots\pi$(arene) interactions are of similar strength to those in 2-(ferrocenyl)thiophene-3-carboxylic acid (Gallagher, Hudson & Manning, 2001) and are relatively weak. Analysis of the hydrogen bonding in (II) reveals that there are only two interactions of significance comprising two C—H$\cdots\pi$ interactions involving the phenyl and imidazolyl rings systems (Fig. 4); details are given in Table 4.

Analysis of the April 2001 version of the Cambridge Structural Database (CSD) using *CONQUEST* (Version 1.2; Allen & Kennard, 1993) for the *para*-anisole group was undertaken for structures which fulfil the three-dimensional coordinates, with $R < 0.10$ and no disorder criteria (see Scheme 2). The C—C$_6$H$_4$OCH$_3$ moiety search gives 767 entries and 1063 observations for C—C—OMe distortions in the range 100–120°; two entries have C—C—OMe angles less than 110° [WIBCEP 102.3° (Niyomura *et al.*, 1999) and ZOYPAE 109.8° (Konda *et al.*, 1995)] and these were omitted from the calculations to give 765 entries and 1060 unique molecular structures. The mean angles are 115.5 and 124.7° about C—C—OMe, which is similar to (I). For example, in tris(4-methoxyphenyl)methanol (HIFVIB; Ferguson *et al.*, 1996), MeO—C—C$_{ortho}$ angles of 115.1 (3)/125.5 (3)° *transoid/cisoid* to the –OCH$_3$ group are distinct and similar to the values of 116/124° reported in the electron diffraction study of anisole, C$_6$H$_5$OCH$_3$ (Siep & Siep, 1973). The mean C—O—CH$_3$ angle from the CSD search is 117.7° (range 110–133°) and the C—C—O—CH$_3$ torsion angle range is −36.9–33.2°, compared with −5.0 (4)° in (I). Analysis of C—C—OMe angles with both greater than 120° shows only one structure (HADVUD; Wey *et al.*, 1993), using identical cut-off criteria, and three structures with both angles less than 120° [JIKXAC (Magnus & Moursounidis, 1991), PEXCOK (Carugo *et al.*, 1993) and ZAMNIK (Mayer *et al.*, 1995)]; however, these latter three structures have R factors greater than 6% and the C—C s.u.'s range from 0.01 to 0.03 Å.
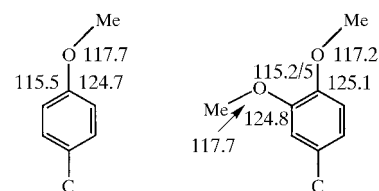
Analysis of the 3,4-veratryl moiety as C—C$_6$H$_3$(OCH$_3$)$_2$ yields 132 entries and 164 unique structures in the CSD. All four C—C—OMe angles were analysed in the range 100–140°. The mean methoxy angles are 115.5 and 125.1° for the *para*-OCH$_3$, and 115.2 and 124.8° for the *meta*-OCH$_3$ groups, with angle ranges typically ±5° of the mean values. The methoxy C—O—CH$_3$ angles are similar, 117.2° for *para*- and 117.7° for *meta*-OCH$_3$, and are also similar to (II). Unusually, there is a structure with both *para*-C—C—OMe angles less than 120° (FAGHIE; Noyori *et al.*, 1986), at 118.9 and 118.1°, and C—O—CH$_3$ angles of 121.5 and 120.3°, and one structure with both *para*-C—C—OMe angles greater than 120° (LOJNED; McAuley & Subramanian, 2000), at 120.2 and 120.2°, and normal C—O—CH$_3$ angles of 118.3 and 118.2°. Analysis of the *meta*-C—O—CH$_3$ angles less than 120° shows MXPMNQ


Figure 2
A view of the molecule of (II) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.
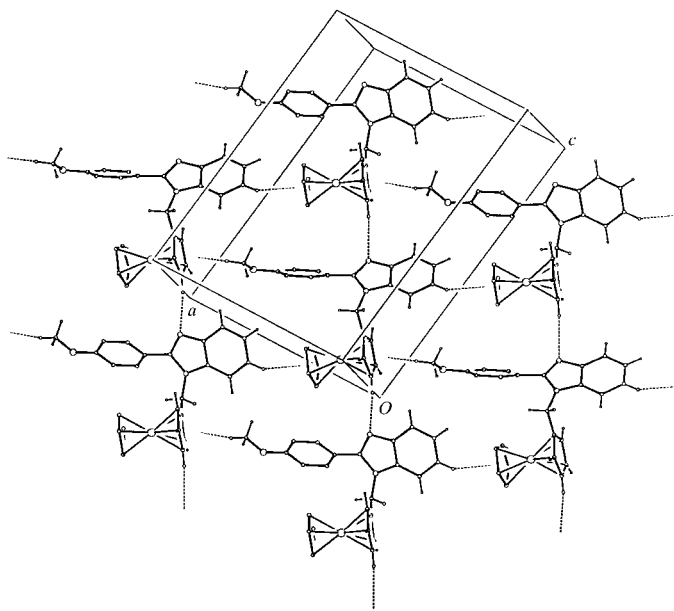
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Figure 3
A view of the interactions in the crystal structure of (I).

(Amatayakul *et al.*, 1979), with values of 117.2 and 114.7°, and 118.3 and 119.6°; however, the *R* factor is 9.3% and the C—C s.u.'s are in the range 0.01–0.03Å. There are no structures with both *meta*-C—O—CH$_3$ angles greater than 120°. Thus, the methoxy angles of 115 and 125° are not unusual for either the methoxy compound, (I), or the dimethoxy derivative, (II).

Analysis of the disposition of the two OCH$_3$ groups relative to one another reveals that for 127 entries (159 unique), the range of C···C distances is narrow, 5.23–5.48 Å, with a mean of 5.40 Å and with the methoxy groups disposed *transoid* to
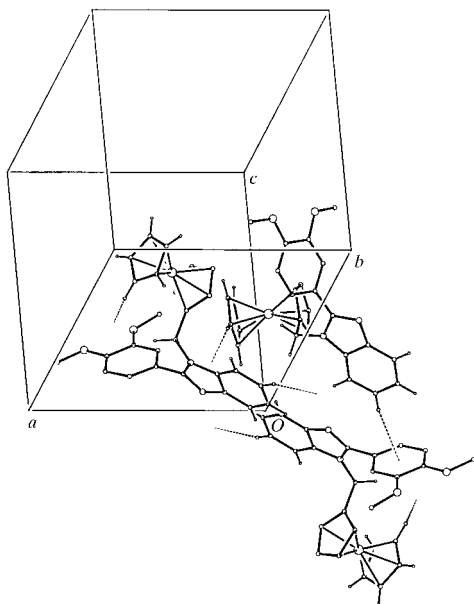

Figure 4
A view of the interactions in the crystal structure of (II).

each other. The five remaining C···C distances are in the range 4.21–4.99 Å and are intermediate between *cisoid* and *transoid*. The analysis suggests that *ortho*-related methoxy groups stagger with respect to one another, with torsion angles to the aromatic ring close to 0°. Analysis of *ortho*-dimethoxy aromatic compounds by angular group-induced bond alternation (AGIBA; Krygowski *et al.*, 1998) indicates some distortion of the C$_6$ aromatic ring geometry in (II); (I) does not display this bond-length alternation.

Extensive structural studies have been reported on the dimethoxyphenyl group in crystal structures (Kumar *et al.*, 1998; Dijksma *et al.*, 1998; Bruno *et al.*, 2001). Steric influences between the CH$_3$ and phenyl-H atoms, or electronic effects involving the oxygen lone pairs (Kumar *et al.*, 1998; Dijksma *et al.*, 1998), have been proposed to account for the planarity of the methoxy groups with the aromatic plane and reported methoxy O—C—C angles, while Bruno *et al.* (2001) have recently commented on the possibility of conjugation effects to determine the planarity of the methoxy groups with the aromatic plane, using combined *ab initio* calculations and database analyses.

Experimental

Compound (I) was prepared as follows: to a mixture of 2-(4-methoxyphenyl)benzimidazole (3.0 g, 12.6 mmol) and K$_2$CO$_3$ (2.61 g, 18.9 mmol) in CH$_3$CN (100 ml) was added (ferrocenylmethyl)trimethylammonium iodide (4.86 g, 12.6 mmol; Pauson *et al.*, 1966; Ferguson *et al.*, 1994), and the mixture was refluxed for 10 h. The reaction was cooled to room temperature, water was added and the suspension extracted into CHCl$_3$. The organic layer was washed with water, dried (MgSO$_4$) and evaporated under vacuum to leave a brown solid. The crude product was purified by column chromatography on silica gel using CH$_2$Cl$_2$/CH$_3$OH (97/3) as eluent. Compound (I) was obtained as a light-orange solid [yield 2.9 g, 54%; m.p. 142–146 K (uncorrected)]. Spectroscopic analysis: IR (KBr, ν, cm^{-1}): 3043, 2981, 2310, 1708, 1609, 1534, 1485, 1460, 1416, 1385, 1323, 1261, 1174, 1106, 1032, 1001, 895, 740, 703; ^{1}H NMR (400 MHz, δH, p.p.m., CDCl$_3$): 7.81 (*m*, 1H, arom-H), 7.71 (*m*, 2H, aryl-H), 7.45 (*m*, 1H, arom-H), 7.30 (*m*, 2H, aryl-H), 7.09 (*m*, 2H, arom-H), 5.21 (*s*, 2H, Fc-CH$_2$) 4.21–4.07 (*m*, 9H, Cp-H), 3.91 (*s*, 3H, aryl-OCH$_3$); ^{13}C NMR (δC, p.p.m., CDCl$_3$): 160.78, 153.47, 142.97, 135.62, 131.03, 122.95, 122.46, 119.6, 114.08, 110.27, 83.3, 68.77, 68.13, 55.42, 44.37.

Compound (II) was prepared as follows: to a mixture of 2-(3,4-dimethoxyphenyl)benzimidazole (5.35 g, 20 mmol) and K$_2$CO$_3$ (4.14 g, 30 mmol) in CH$_3$CN (150 ml) was added (ferrocenyl-methyl)trimethylammonium iodide (8.1 g, 21 mmol; Pauson *et al.*, 1966; Ferguson *et al.*, 1994) and the mixture refluxed for 16 h. The work-up was similar to that described for (I) above. Compound (II) was obtained as a brown oil which later solidified [yield 1.8 g, 38%; m.p. 192–194 K (uncorrected)]. Spectroscopic analysis: IR (KBr, ν, cm^{-1}): 3051, 2982, 2849, 2697, 2411, 2320, 1713, 1609, 1495, 1434, 1420, 1363, 1259, 1145, 1024, 898, 743, 709; ^{1}H NMR (400 MHz, δH, p.p.m., CDCl$_3$): 7.81 (*m*, 1H, arom-H), 7.51 (*m*, 1H, arom-H), 7.35–7.03 (*m*, 5H, aryl-H and arom-H), 5.24 (*s*, 2H, Fc-CH$_2$), 4.15–4.09 (*m*, 9H, Cp Fc-H), 4.00 (*s*, 3H, OCH$_3$), 3.94 (*s*, 3H, OCH$_3$); ^{13}C NMR (δC, p.p.m., CDCl$_3$): 153.84, 150.75, 149.51, 136.08, 123.05, 122.84, 122.55, 120.07, 113.21, 111.08, 110.69, 83.86, 69.25, 69.08, 68.57, 56.55, 56.43, 44.89.

Compound (I)

Crystal data

$[Fe(C_5H_5)(C_{20}H_{17}N_2O)]$	$D_x = 1.389$ Mg m^{-3}
$M_r = 422.30$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 75
$a = 12.4326 (10)$ Å	reflections
$b = 9.5414 (7)$ Å	$\theta = 2.4$–$15.6°$
$c = 17.1682 (8)$ Å	$\mu = 0.77$ mm^{-1}
$\beta = 97.400 (5)°$	$T = 294 (1)$ K
$V = 2019.6 (2)$ Å^3	Block, orange
$Z = 4$	$0.43 \times 0.33 \times 0.30$ mm

Data collection

Siemens $P4$ diffractometer	$R_{int} = 0.011$
ω scans	$\theta_{max} = 28°$
Absorption correction: ψ scan	$h = -16 \rightarrow 1$
(North *et al.*, 1968)	$k = -1 \rightarrow 12$
$T_{min} = 0.737$, $T_{max} = 0.803$	$l = -22 \rightarrow 22$
6105 measured reflections	3 standard reflections
4830 independent reflections	every 197 reflections
3693 reflections with $I > 2\sigma(I)$	intensity variation: $\pm 1\%$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.055P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 0.456P]$
$wR(F^2) = 0.110$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
4830 reflections	$\Delta\rho_{max} = 0.58$ e Å^{-3}
263 parameters	$\Delta\rho_{min} = -0.31$ e Å^{-3}
H-atom parameters constrained	

Compound (II)

Crystal data

$[Fe(C_5H_5)(C_{21}H_{19}N_2O_2)]$	$D_x = 1.415$ Mg m^{-3}
$M_r = 452.32$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/a$	Cell parameters from 50
$a = 11.7089 (10)$ Å	reflections
$b = 13.7888 (12)$ Å	$\theta = 9.0$–$37.9°$
$c = 13.2441 (11)$ Å	$\mu = 0.74$ mm^{-1}
$\beta = 96.758 (7)°$	$T = 294 (2)$ K
$V = 2123.4 (3)$ Å^3	Block, red
$Z = 4$	$0.35 \times 0.25 \times 0.15$ mm

Data collection

Siemens $P4$ diffractometer	$R_{int} = 0.028$
ω scans	$\theta_{max} = 28°$
Absorption correction: ψ scan	$h = -1 \rightarrow 15$
(North *et al.*, 1968)	$k = -1 \rightarrow 18$
$T_{min} = 0.783$, $T_{max} = 0.900$	$l = -17 \rightarrow 17$
6262 measured reflections	3 standard reflections
5088 independent reflections	every 197 reflections
3684 reflections with $I > 2\sigma(I)$	intensity variation: $\pm 1\%$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.04P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$+ 0.537P]$
$wR(F^2) = 0.096$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
5088 reflections	$\Delta\rho_{max} = 0.21$ e Å^{-3}
282 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}
H-atom parameters constrained	

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

O1—C34	1.373 (2)	N2—C2	1.457 (2)
O1—C37	1.418 (3)	N2—C3	1.384 (2)
N1—C1	1.321 (2)	C1—C31	1.471 (2)
N1—C4	1.381 (2)	C2—C11	1.502 (3)
N2—C1	1.382 (2)		
O1—C34—C33	125.0 (2)	N1—C1—C31	122.62 (17)
O1—C34—C35	115.1 (2)	N2—C1—C31	125.14 (16)
C34—O1—C37	117.7 (2)	N2—C2—C11	112.75 (15)
C1—N1—C4	105.47 (15)	N2—C3—C4	105.59 (16)
C1—N2—C2	130.00 (15)	N2—C3—C8	131.71 (18)
C1—N2—C3	106.46 (15)	N1—C4—C3	110.25 (16)
C2—N2—C3	123.24 (15)	N1—C4—C5	129.89 (19)
N1—C1—N2	112.23 (16)	C2—C11—Fe1	126.56 (13)
N2—C2—C11—Fe1	−109.58 (16)	N1—C1—C31—C32	38.0 (3)
C1—N2—C2—C11	104.5 (2)	C37—O1—C34—C33	−5.0 (4)

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

O1—C33	1.368 (3)	N2—C1	1.378 (3)
O1—C37	1.432 (3)	N2—C2	1.466 (3)
O2—C34	1.364 (3)	N2—C3	1.383 (3)
O2—C38	1.423 (3)	C1—C31	1.475 (3)
N1—C1	1.317 (3)	C2—C11	1.498 (3)
N1—C4	1.388 (3)		
O1—C33—C32	124.6 (2)	N1—C1—N2	112.98 (19)
O1—C33—C34	115.9 (2)	N1—C1—C31	123.47 (19)
C33—O1—C37	116.5 (2)	N2—C1—C31	123.55 (19)
O2—C34—C33	115.7 (2)	N2—C2—C11	112.21 (18)
O2—C34—C35	125.1 (2)	N2—C3—C4	105.50 (18)
C34—O2—C38	116.7 (2)	N2—C3—C8	132.6 (2)
C1—N1—C4	104.98 (17)	N1—C4—C3	110.14 (19)
C1—N2—C2	126.63 (19)	N1—C4—C5	129.7 (2)
C1—N2—C3	106.38 (17)	C2—C11—Fe1	125.74 (15)
C2—N2—C3	126.32 (18)		
N2—C2—C11—Fe1	179.65 (15)	C37—O1—C33—C32	11.2 (4)
N1—C1—C31—C32	67.3 (3)	C38—O2—C34—C35	4.7 (4)

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

$Cg1$ and $Cg2$ are the centroids of the $\eta^5(C_5H_4)$ and $\eta^5(C_5H_5)$ rings, respectively.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C13—H13$\cdots$N1^i	0.93	2.48	3.397 (3)	168
C2—H2$B\cdots$N1^{ii}	0.97	2.61	3.404 (3)	139
C7—H7$\cdots Cg1^{iii}$	0.93	2.81	3.644 (3)	151
C37—H37$B\cdots Cg2^{iv}$	0.96	2.85	3.734 (3)	154

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

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

$Cg1$ and $Cg2$ are the centroids of the $\eta^5(C_5H_4)$ and $\eta^5(C_5H_5)$ rings, respectively.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C21—H21$\cdots Cg1^i$	0.93	2.88	3.514 (3)	127
C7—H7$\cdots Cg2^{ii}$	0.93	2.73	3.636 (3)	163

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

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Molecules (I) and (II) crystallized in the monoclinic system; space groups $P2_1/n$ and $P2_1/a$ were assumed from the systematic absences and confirmed by the analyses. All H atoms bound to C atoms were treated as riding with *SHELXL*97 defaults (Sheldrick, 1997) for C—H distances, and with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and $1.2U_{eq}(C)$ for the remainder.

For both compounds, data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *PLATON* (Spek, 1998); software used to prepare material for publication: *SHELXL*97 and *PREP*8 (Ferguson, 1998).

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