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Monohalogenated ferrocenes $C_5H_5FeC_5H_4X$ (X = Cl, Br and I) and a second polymorph of $C_5H_5FeC_5H_4I$

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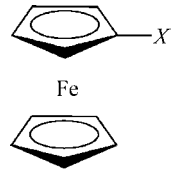
The structures of the three title monosubstituted ferrocenes, namely 1-chloroferrocene, [Fe(C_5H_5)(C_5H_4Cl)], (I), 1-bromoferrocene, [Fe(C_5H_5)(C_5H_4Br)], (II), and 1-iodoferrocene, [Fe(C_5H_5)(C_5H_4I)], (III), were determined at 100 K. The chloro- and bromoferrocenes are isomorphous crystals. The new triclinic polymorph [space group $P\overline{1}$, $Z = 4$, $T = 100$ K, $V = 943.8\ (4)$ Å^3] of iodoferrocene, (III), and the previously reported monoclinic polymorph of (III) [Laus, Wurst & Schottenberger (2005). *Z. Kristallogr. New Cryst. Struct.* **220**, 229–230; space group Pc, $Z = 4$, $T = 100$ K, $V = 924.9$ Å^3] were obtained by crystallization from ethanolic solutions at 253 and 303 K, respectively. All four phases contain two independent molecules in the unit cell. The relative orientations of the cyclopentadienyl (Cp) rings are eclipsed and staggered in the independent molecules of (I) and (II), while (III) demonstrates only an eclipsed conformation. The triclinic and monoclinic polymorphs of (III) contain nonbonded intermolecular I···I contacts, causing different packing modes. In the triclinic form of (III), the molecules are arranged in zigzag tetramers, while in the monoclinic form the molecules are arranged in zigzag chains along the a axis. Crystallographic data for (III), along with the computed lattice energies of the two polymorphs, suggest that the monoclinic form is more stable.

Comment

Once ferrocene had been synthesized, numerous applications were found for the compound and its derivatives. Many ferrocene-based materials were used in the development of bioorganometallic chemistry (Staveren & Metzler-Nolte, 2004), catalysis (Togni & Hayashi, 1995), dendrimers (Astruc *et al.*, 2008), nonlinear optical materials (Kinnibrugh *et al.*, 2009), anticancer agents (Jaouen, 2008), *etc*. For example, ferroquine has been perceived to be extremely active against a chloroquine-resistant strain CQ(−) of *Plasmodium falciparum* (Dubar *et al.*, 2008). In this work, we report the first structural study of the monohalogen-substituted ferrocenes 1-chloroferrocene, (I), and 1-bromoferrocene, (II), and a triclinic form of 1-iodoferrocene, (III). It is surprising that the elucidation of the structures of the substituted ferrocenes presented here had not been carried out before, although this is probably due to experimental difficulties related to the low melting points of these compounds. All the title compounds contain two crystallographically independent molecules, denoted A and B, in the unit cell.



(I) X = Cl
(II) X = Br
(III) X = I

Disorder of the Cp rings in ferrocene is a well known phenomenon (Seiler & Dunitz, 1979). Previous workers have found a dynamic type of disorder for the metallocenes Cp_2Co and Cp_2V (Cp is cyclopentadienyl; Antipin *et al.*, 1993; Antipin & Boese, 1996). Usually, monosubstituted ferrocenes do not show disorder, due to higher rotational barriers compared with unsubstituted Cp rings (Sato, Iwai *et al.*, 1984). Nevertheless, we found that compound (I) has disordered Cp rings for molecule B with equal occupancies over the two orientations at 100 K. A disorder model for the C_5H_5 and C_5H_4Cl rings of molecule B was proposed, with the two orientations of each ring differing by rotations in the ring plane of about 20 and 16°, respectively.

The mean values of the Fe—C, C—C, C—X (X = Cl, Br or I) and Fe···Cg (Cg is a ring centroid) bond lengths, and the η^5-C_5H_4X/η^5-C_5H_5 angles for molecules (I), (II) and (III) are presented in Table 1. The Fe—C and Fe···Cg distances to the substituted η^5-C_5H_4X ring are slightly shorter than those for the η^5-C_5H_5 ring, which is attributed to the substituent in the η^5-C_5H_4X ring. The shortening of these distances in (I)–(III) is statistically not significant but this trend was observed for all other monosubstituted ferrocenes, whether the substituent is an electron-donating or an electron-withdrawing group (Kaluski & Struchkov, 1966; Sato, Iwai *et al.*, 1984; Sato, Katada *et al.*, 1984; Drouin *et al.*, 1997; Foucher *et al.*, 1999; Lin *et al.*, 1998; Alley & Henderson, 2001; Hnetinka *et al.*, 2004; Nemykin *et al.*, 2007; Gasser *et al.*, 2007).

The rings of (I) are eclipsed in molecule A, with the torsion angle C1A(Cl)···Cg1···Cg2···C6A = −2.90 (11)°. Molecule B exists in two different conformations. The Cp rings of compound (II) are eclipsed in molecule A and staggered for molecule B; the torsion angles C1A(Br1A)···Cg1···Cg2···C6A and C1B(Br1B)···Cg3···Cg4···C6B are −2.6 (11) and −29.2 (11)°, respectively. The rings of compound (III) are in an eclipsed conformation in both independent

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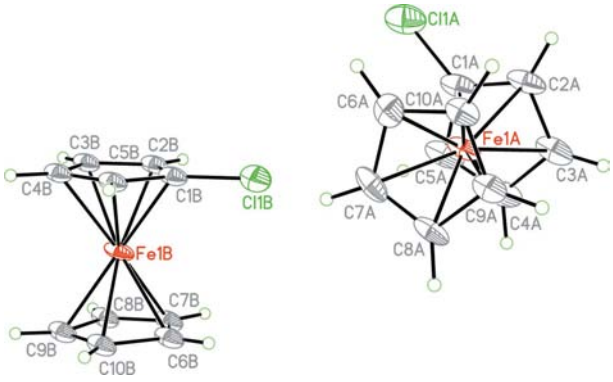

Figure 1
The two independent molecules of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The second disorder component of molecule *B* has been omitted for clarity.

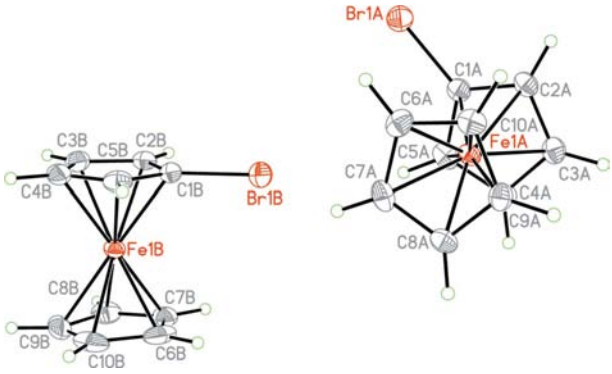

Figure 2
The two independent molecules of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

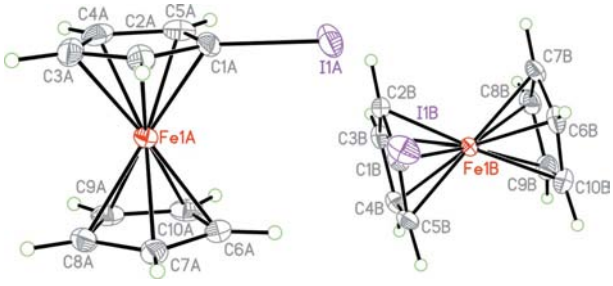

Figure 3
The two independent molecules of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

molecules; the torsion angles C1*A*(I1*A*)···*Cg*1···*Cg*2···C6*A* and C1*B*(I1*B*)···*Cg*3···*Cg*4···B are −2.2 (11) and −1.9 (11), respectively. The η^5-C_5H_4X and η^5-C_5H_5 rings are almost parallel in the molecules of (I), (II) and (III) (Figs. 1, 2 and 3, and Table 1).

Crystals of (I) and (II) obtained from ethanolic solutions are monoclinic and isomorphous. In these crystal structures, four molecules form tetramers *via* intermolecular C—H···*X* (*X* = Cl or Br) hydrogen bonds between the C—H groups of

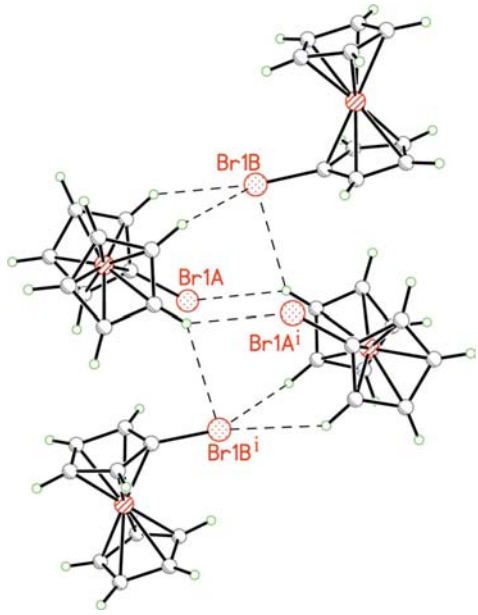

Figure 4
A view of the tetramer in the structure of (II). [Symmetry code: (i) $1-x$, $1-y$, $1-z$.]

molecules with eclipsed conformations and the *X* atoms of molecules with staggered conformations, and also C—H···*X* hydrogen bonds between molecules with eclipsed conformations (Fig. 4 and Table 2). These tetramers are, in turn, linked to each other by weak C—H···π interactions along the *a* axis.

The new triclinic polymorph of (III) [space group $P\overline{1}$, $Z = 4$, $T = 100$ K, $V = 943.8\ (4)$ Å^3] and the previously reported monoclinic polymorph (space group *Pc*, $Z = 4$, $T = 100$ K, $V = 924.9$ Å^3) (Laus *et al.*, 2005) were obtained upon crystallization of ethanol solutions at 253 and 303 K, respectively. Crystals of another previously reported monoclinic polymorph (space group *Pc*, $Z = 4$, $T = 228$ K, $V = 953.7$ Å^3) were grown by vacuum sublimation (Laus *et al.*, 2005). Since this previously reported structure was studied at 228 K, we obtained X-ray diffraction data for both polymorphs of (III) at 100 K and their comparison is based on these data. Both forms contain two crystallographically independent molecules (*A* and *B*). The bond lengths and angles in both polymorphs are very similar. The molecular conformations are eclipsed for the triclinic polymorph of (III), and deviate slightly from an eclipsed conformation in the monoclinic polymorph; the torsion angles C1*A*(I1*A*)···*Cg*1···*Cg*2···C6*A* and C1*B*(I1*B*)···*Cg*3···*Cg*4···C6*B* are −4.8 (11) and 7.0 (11)°, respectively.

The triclinic and monoclinic polymorphs of (III) both contain short nonbonded intermolecular I···I contacts but have different molecular packing modes. The two pairs of independent molecules *A* and *B* in triclinic (III) form zigzag tetramers *via* I···I contacts [I1*A*···I1*B* = 4.129 (1) Å and C1*A*—I1*A*···I1*B* = 150.78 (10)°; I1*B*··· I1*B*^{iii} = 4.123 (1) Å, C1*B*—I1*B*···I1*B*^{iii} = 136.71 (9)° and I1*A*—I1*B*··· I1*B*^{iii} = 71.07 (10)°; symmetry code: (iii) $1-x$, $2-y$, $1-z$] (Fig. 5). These I···I contacts are longer than the sum of spherical van der Waals radii proposed by Bondi (3.96 Å; Bondi, 1964; Rowland & Taylor, 1996), but shorter than the sum of spher-

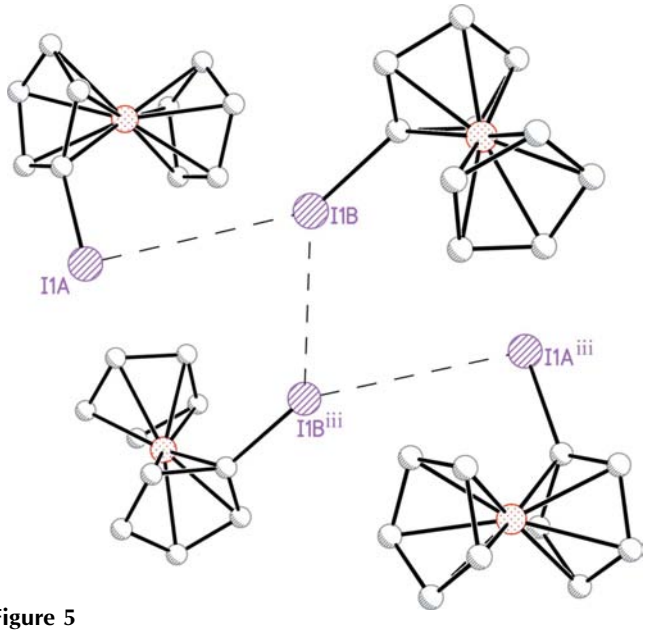

Figure 5
A view of the tetramer in the structure of triclinic (III). Dashed lines indicate the I···I contacts. [Symmetry code: (iii) $1-x, 2-y, 1-z$.]

oidal van der Waals radii for I (4.26 Å; Nyburg & Faerman, 1985). The I atoms of molecules *B* demonstrate fork-type I···I interactions, while the I atoms of molecules *A* possess only one I···I contact. All four I···I contacts form an almost planar zigzag tetramer.

Molecules in the monoclinic form of (III) are arranged in chains along the *a* axis connected by zigzag I···I contacts [I1*A*···I1*B* = 4.183 (1) Å and C1*A*—I1*A*···I1*B* = 155.3 (8)°; I1*B*··· I1*A*^{ii} = 3.913 (1) Å, C1*B*—I1*B*···I1*A*^{ii} = 93.7 (1)° and I1*A*—I1*B*···I1*A*^{ii} = 101.9 (1)°; symmetry code: (ii) $-1+x, y, z$] (Fig. 6). The I···I contacts between independent molecules *A* and *B* are shorter than the sum of the van der Waals radii proposed by Bondi, while the I···I contacts which connect pairs of molecules *B* and *A*# (Fig. 6) are somewhat longer than the sum of van der Waals radii proposed for spherical and somewhat shorter than for spheroidal I atoms. The lengths of the I···I contacts vary for the monoclinic polymorph from those of the triclinic by *ca* 0.2 Å, while the angles differ significantly.

The tetramers in triclinic (III) and the zigzag chains in monoclinic (III) are linked to each other by weak C—H···π interactions (Table 3). The intermolecular C—H···π(C_5H_5) contacts for the monoclinic polymorph of (III) are approximately the same as for the triclinic polymorph. In the case of the monoclinic polymorph of (III), there are C—H···I hydrogen bonds between neighbouring molecules in the zigzag chains (Table 2), while the I atoms of the triclinic polymorph of (III) do not participate in hydrogen bonding.

We evaluated the crystal energies of the two polymorphs of (III) using the *Cerius*^{2} program (Molecular Simulations, 1999). Crystal energies were calculated using the Dreiding force field (Mayo *et al.*, 1990). The initial crystal energies were −16.8 and −18.4 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}) and the energies after minimization were −17.9 and −18.9 kcal mol^{-1}

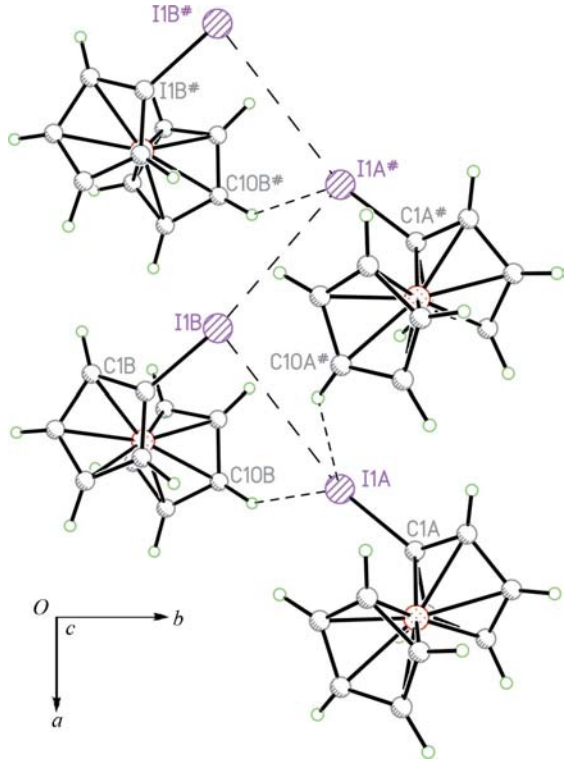

Figure 6
A view of the zigzag chain for monoclinic (III). Dashed lines indicate the I···I contacts and C—H···I hydrogen bonds. [Symmetry code: (ii) $-1+x, y, z$.]

for the triclinic and monoclinic polymorphs, respectively. These results, along with data on the densities of the polymorphs and their unit-cell volumes, lead us to suggest that the noncentrosymmetric monoclinic polymorph is more stable than the triclinic one.

Experimental

Compounds (I), (II) and (III) were prepared according to standard literature procedures (Fish & Rosenblum, 1965; Perevalova, 1972). Slow evaporation from ethanol solutions produced yellow crystals of (I) and brown crystals of (II). The triclinic and monoclinic polymorphs of (III) were obtained as yellow and orange crystals, respectively, upon crystallization from ethanol solutions at 253 and 303 K, respectively. During crystal selection on the stage of a polarizing microscope, crystals of (I) and (II) melted rapidly due to their low melting points and the heat produced by the microscope lamp. To avoid this problem we used a microscope cooling stage (INSTEC) for crystal selection.

Compound (I)

Crystal data

$[Fe(C_5H_5)(C_5H_4Cl)]$
M_r = 220.47
Monoclinic, $P2_1/c$
a = 7.5068 (16) Å
b = 11.303 (3) Å
c = 20.444 (4) Å
β = 90.041 (5)°
V = 1734.6 (7) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 1.98 mm^{-1}
T = 100 K
0.16 × 0.10 × 0.04 mm

Table 1
Mean values of the geometric parameters (Å, °) for (I), (II), triclinic (III) and monoclinic (III) at 100 K.

Cp′ is the C_5H_4X ring and Cp is the C_5H_5 ring. *Cg*1 and *Cg*2 are the centroids of the η^5-C_5H_4X and η^5-C_5H_5 rings, respectively.

	(I*A*)	(I*B*)	(II*A*)	(II*B*)
C—C for Cp′	1.422 (6)	1.422 (10)	1.426 (3)	1.422 (3)
C—C for Cp	1.420 (6)	1.422 (10)	1.426 (3)	1.414 (4)
Fe—C for Cp′	2.039 (4)	2.044 (7)	2.040 (2)	2.041 (2)
Fe—C for Cp	2.044 (4)	2.047 (6)	2.049 (2)	2.047 (3)
C—*X*	1.733 (5)	1.708 (7)	1.894 (2)	1.882 (2)
Fe—*Cg*1	1.646 (12)	N/A	1.640 (1)	1.644 (1)
Fe—*Cg*2	1.653 (12)	N/A	1.651 (1)	1.656 (1)
C_5H_4X/C_5H_5 angle	0.91 (11)		1.07 (15)	2.68 (14)

	(III*A*), triclinic	(III*B*), triclinic	(III*A*), monoclinic	(III*B*), monoclinic
C—C for Cp′	1.430 (5)	1.428 (5)	1.418 (6)	1.423 (5)
C—C for Cp	1.425 (5)	1.428 (5)	1.417 (6)	1.418 (5)
Fe—C for Cp′	2.044 (3)	2.040 (3)	2.041 (3)	2.039 (3)
Fe—C for Cp	2.048 (3)	2.047 (3)	2.045 (4)	2.044 (3)
C—*X*	2.084 (3)	2.088 (3)	2.092 (3)	2.091 (3)
Fe—*Cg*1	1.642 (1)	1.639 (1)	1.646 (1)	1.641 (1)
Fe—*Cg*2	1.651 (1)	1.648 (1)	1.652 (1)	1.650 (1)
C_5H_4X/C_5H_5 angle	0.68 (19)	1.0 (2)	1.1 (1)	0.2 (1)

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.743, T_{max} = 0.925
18849 measured reflections
4596 independent reflections
3666 reflections with $I > 2\sigma(I)$
R_{int} = 0.056

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.114
S = 1.00
4596 reflections
221 parameters
48 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.74 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

Compound (II)

Crystal data

$[Fe(C_5H_5)(C_5H_4Br)]$
M_r = 264.93
Monoclinic, $P2_1/c$
a = 7.5222 (14) Å
b = 11.613 (2) Å
c = 20.440 (4) Å
β = 90.050 (3)°
V = 1785.5 (6) Å^3
Z = 8
Mo *Kα* radiation
μ = 6.10 mm^{-1}
T = 100 (2) K
0.16 × 0.10 × 0.04 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: numerical (*APEX2*; Bruker, 2005)
T_{min} = 0.442, T_{max} = 0.793
23171 measured reflections
4504 independent reflections
3816 reflections with $I > 2\sigma(I)$
R_{int} = 0.052

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.078
S = 1.02
4504 reflections
217 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.60 e Å^{-3}
$\Delta\rho_{min}$ = −0.70 e Å^{-3}

Table 2
Intermolecular C—H···*X* (*X* = Cl, Br or I) hydrogen bonds (Å, °) in (I), (II) and monoclinic (III).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
Compound (I)				
C7*A*—H7*AA*···Cl1*B*	1.00	2.69	3.548 (7)	145
C5*A*—H5*AA*···Cl1′	1.00	2.80	3.661 (8)	144
C6*A*—H6*AA*···Cl1*B*^{i}	1.00	2.88	3.592 (5)	144
Compound (II)				
C7*A*—H7*AA*···Br1*B*	1.00	2.95	3.769 (3)	140
C5*A*—H5*AA*···Br1*B*	1.00	3.04	3.825 (3)	136
C6*A*—H6*AA*···Br1*A*^{i}	1.00	3.00	3.619 (2)	121
C6*A*—H6*AA*···Br1*B*^{i}	1.00	3.04	3.860 (2)	140
Compound (III), monoclinic				
C10*A*—H10*A*···I1*A*^{ii}	1.00	3.24	4.094 (5)	144
C10*B*—H10*B*···I1*A*	1.00	3.21	4.038 (5)	140

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

Table 3
C—H···π(C_5H_5) short-contact geometry (Å) for the triclinic and monoclinic forms of (III).

Centroids are considered to be the middle of the corresponding C═C bonds.

Triclinic (III)			
C4*B*—H4*BA*···C4*A*^{v}	2.73	C3*A*—H3*AA*···C3*B*^{i}	2.80
C4*B*—H4*BA*···centroid	2.67	C3*A*—H3*AA*···C4*B*^{i}	2.70
C3*A*—H3*AA*···centroid	2.65		
Monoclinic (III)			
C8*A*—H8*AA*···C2*B*^{i}	2.74	C3*A*—H3*AA*···C9*B*^{vi}	2.64
C8*A*—H8*AA*···C3*B*^{i}	2.99	C3*A*—H3*AA*···C10*B*^{vi}	2.80
C8*A*—H8*AA*···centroid	2.78	C3*A*—H3*AA*···centroid	2.63
C7*A*—H7*AA*···C6*B*^{iii}	2.88	C3*B*—H3*BA*···C9*A*^{vii}	2.69
C7*A*—H7*AA*···C10*B*^{iii}	2.73	C3*B*—H3*BA*···C10*A*^{vii}	2.93
C7*A*—H7*AA*···centroid	2.71	C3*B*—H3*BA*···centroid	2.72
C2*B*—H2*BA*···C9*A*^{iv}	2.77	C4*B*—H4*BA*···C2*A*^{viii}	2.89
C2*B*—H2*BA*···C10*A*^{iv}	2.81	C4*B*—H4*BA*···C3*A*^{viii}	2.92
C2*B*—H2*BA*···centroid	2.70	C4*B*—H4*BA*···centroid	2.82
C4*B*—H4*BA*···C3*A*^{v}	2.80		

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

Compound (III), triclinic polymorph

Crystal data

$[Fe(C_5H_5)(C_5H_4I)]$
M_r = 311.92
Triclinic, $P\overline{1}$
a = 7.6372 (19) Å
b = 11.371 (3) Å
c = 11.694 (3) Å
α = 72.220 (3)°
β = 80.196 (3)°
γ = 79.577 (3)°
V = 943.8 (4) Å^3
Z = 4
Mo *Kα* radiation
μ = 4.81 mm^{-1}
T = 100 K
0.40 × 0.30 × 0.20 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.181, T_{max} = 0.373
13091 measured reflections
4676 independent reflections
4314 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.083
S = 1.01
4676 reflections
217 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.66 e Å^{-3}
$\Delta\rho_{min}$ = −1.89 e Å^{-3}

Compound (III), monoclinic polymorph

Crystal data

$[Fe(C_5H_5)(C_5H_4I)]$	V = 924.9 (2) Å^3
M_r = 311.92	Z = 4
Monoclinic, Pc	Mo $K\alpha$ radiation
a = 6.2918 (10) Å	μ = 4.91 mm^{-1}
b = 9.7229 (15) Å	T = 100 K
c = 15.146 (2) Å	0.14 × 0.11 × 0.09 mm
β = 93.437 (2)°	

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	8464 measured reflections 3972 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	3900 reflections with $I > 2\sigma(I)$
T_{min} = 0.529, T_{max} = 0.638	R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.018	H-atom parameters constrained
$wR(F^2)$ = 0.041	$\Delta\rho_{max}$ = 0.66 e Å^{-3}
S = 1.01	$\Delta\rho_{min}$ = −0.47 e Å^{-3}
3972 reflections	Absolute structure: Flack (1983), with 1954 Friedel pairs
217 parameters	Flack parameter: 0.003 (18)
2 restraints	

All H atoms were positioned geometrically, with C—H = 1.00 Å, and refined in riding mode, with U_{iso}(H) = 1.2U_{eq}(C). The crystals of (I) were found to be twinned. The structure of (I) was refined by the method of Pratt *et al.* (1971) and Jameson (1982), with a TWIN matrix defined as (100/0$\bar{1}$0/00$\bar{1}$), which is the default for a monoclinic twinning type with β close to 90° and a twin fraction of 0.380 (1). A disorder model for the C_5H_5 and C_5H_4Cl rings was found with two orientations of the rings with equal occupancies for the two positions, differing by rotations in the ring plane of about 20 and 16°, respectively. The C atoms of the disordered C_5H_5 and C_5H_4Cl rings of molecule *B* of (I) were restrained to be planar within 0.001 Å. The distances between C atoms were fixed in a pentagon fashion at 1.425 (1) and 2.300 (1) Å for 1,2- and 1,3-distances, respectively. The 33 reflections which did not agree with the ideal model of the disordered molecule were omitted from the refinement.

For all compounds, data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3110). Services for accessing these data are described at the back of the journal.

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