metal-organic papers

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.006 Å
R factor = 0.037
wR factor = 0.094
Data-to-parameter ratio = 24.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

1,1'-Dibromoferrocene

The structure of 1,1'-dibromoferrocene, [Fe(C$_5$H$_4$Br)$_2$], has been determined by single-crystal X-ray diffraction at 100 K. The two Br substituents are eclipsed in the solid state, with a Br$\cdots$Br distance of 3.6172 (6) Å.

Comment

The solid state structure of 1,1'-dibromoferrocene, (I), a versatile starting material for a wide range of disubstituted ferrocene derivatives, has been determined at 100 K. It was found to crystallize in the non-centrosymmetric space group $P2_1$. The crystal under investigation was a racemic twin, with a ratio of 88:12 (1) for the two components.

(I)
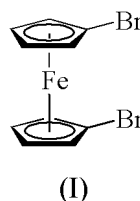
Despite the steric demand of the two bromine substituents, the two cyclopentadienyl (Cp) rings are found to exhibit an eclipsed conformation in the solid state. The pseudo-torsion angle of the two Br atoms (defined by way of the two Cp-ring centroids) is only 1.55 (1)°, thus forcing the two Br atoms into close proximity, with a Br$\cdots$Br distance of only 3.6172 (6) Å. The resulting steric strain forces the two halogen atoms away from one another and they are pushed out of the planes defined the Cp C atoms by 0.137 (6) and 0.082 (6) Å. The Cp rings themselves are less affected. They are not significantly bent and are still nearly parallel to each other, with an angle of only 2.1 (3)° between the planes defined by the C atoms. The angle at the iron center (as defined by the two ring centroids) is 177.71 (4)°, and the distances of the Fe atom to the ring centroids are 1.6500 (5) and 1.6483 (5) Å. The solid-state structures of two other 1,1'-dibromoferrocenes, both with additional phosphine ligands, have been reported to date (Butler *et al.*, 1999; Hursthouse *et al.*, 2003). In both cases, the Br atoms are eclipsed, not with the other Br but with an H substituent on the second ring. Thus, the conformational arrangement found here for 1,1'-dibromoferrocene seems not to be the result of a general electronic preference within this class of compounds, but has to be attributed to crystal packing effects in the solid state.

Experimental

1,1'-Dibromoferrocene was isolated when attempting to synthesize 1,1'-dicyanoferrocene from 1,1'-dilithioferrocene and cyanogen

bromide (Boev & Dombrovskii, 1976). Solid 1,1′-dilithioferrocene TMEDA disolvate (TMEDA is *N,N,N′,N′*-tetramethylethylene-diamine; 2.770 g, 6.437 mmol) was suspended in toluene (50 ml) and cooled to 195 K under a dry nitrogen atmosphere. A solution of cyanogen bromide (1.500 g, 14.16 mmol) in toluene (35 ml) was added *via* a cannula and the mixture was stirred overnight, gradually warming to ambient temperature. The mixture was heated to reflux for 3 h and poured over 500 g of ice, yielding a yellow solid. The mixture was allowed to melt and the toluene layer was separated, dried over MgSO₄ and dried *in vacuo*. The crude product was dissolved in a minimum of warm ethanol and placed in a freezer overnight. A light-orange compound was isolated by filtration and was identified as 1,1′-dibromoferrocene (0.540 g, 24.4%). The filtrate was layered with petroleum ether and left to evaporate slowly in air. Large irregular shaped orange–brown crystals of 1,1′-dibromo-ferrocene were isolated, cut to a reasonable size, and analysed by X-ray crystallography.

Crystal data

[Fe(C₅H₄Br)₂]	$D_x = 2.357$ Mg m^{-3}
$M_r = 343.83$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 5466
$a = 6.2289$ (6) Å	reflections
$b = 10.024$ (1) Å	$\theta = 2.6$–31.9°
$c = 7.8351$ (8) Å	$\mu = 9.75$ mm^{-1}
$\beta = 97.987$ (2)°	$T = 100$ (2) K
$V = 484.49$ (8) Å³	Irregular fragment, orange–brown
$Z = 2$	$0.50 \times 0.36 \times 0.31$ mm

Data collection

Bruker SMART APEX CCD	2890 independent reflections
diffractometer	2850 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.022$
Absorption correction: multi-scan	$\theta_{max} = 30.5°$
(*SADABS* in *SAINT-Plus*;	$h = -8 \rightarrow 8$
Bruker, 2003)	$k = -14 \rightarrow 14$
$T_{min} = 0.021$, $T_{max} = 0.05$	$l = -11 \rightarrow 10$
5736 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0733P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$+ 0.3107P]$
$wR(F^2) = 0.095$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
2890 reflections	$\Delta\rho_{max} = 1.12$ e Å^{-3}
119 parameters	$\Delta\rho_{min} = -0.66$ e Å^{-3}
H-atom parameters constrained	Absolute structure: Flack (1983),
	1339 Friedel pairs
	Flack parameter = 0.116 (13)

Table 1
Selected geometric parameters (Å, °).

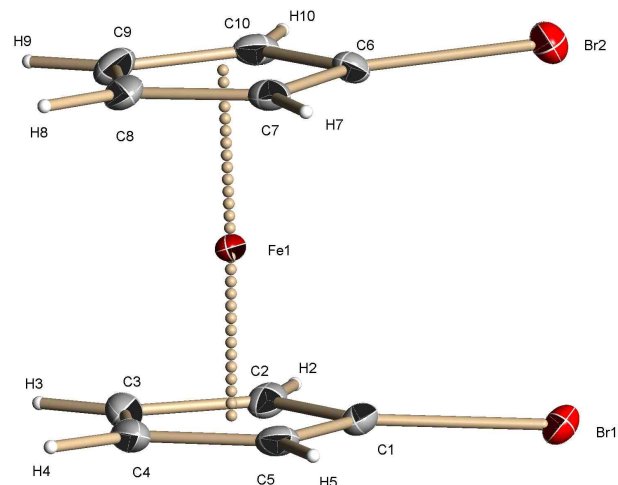|			
Br1—C1	1.882 (4)	C5—Fe1	2.051 (4)
Br2—C6	1.866 (4)	C6—C10	1.428 (5)
C1—C2	1.423 (6)	C6—C7	1.433 (5)
C1—C5	1.431 (6)	C6—Fe1	2.042 (4)
C1—Fe1	2.035 (4)	C7—C8	1.419 (6)
C2—C3	1.431 (6)	C7—Fe1	2.048 (4)
C2—Fe1	2.054 (4)	C8—C9	1.429 (7)
C3—C4	1.428 (7)	C8—Fe1	2.048 (4)
C3—Fe1	2.052 (4)	C9—C10	1.425 (6)
C4—C5	1.430 (6)	C9—Fe1	2.046 (4)
C4—Fe1	2.048 (4)		
C2—C1—Br1	126.2 (3)	C10—C6—Br2	125.0 (3)
C5—C1—Br1	124.0 (3)	C7—C6—Br2	125.7 (3)

Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids, with H atoms drawn as spheres of arbitrary radius.

H atoms were positioned geometrically with a C—H distance of 0.95 Å and were refined with $U_{iso}(H) = 1.2U_{eq}(C)$. The s.u. values of the cell parameters are taken from the software, recognizing that the values are unreasonably small (Herbstein, 2000). The highest peak in the electron-density map was 0.04 Å from atom Fe1.

Data collection: *SMART* (Bruker, 1997–2002); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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