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(*E*)-1-(4-Bromobenzylidene)ferrocene

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Key indicators

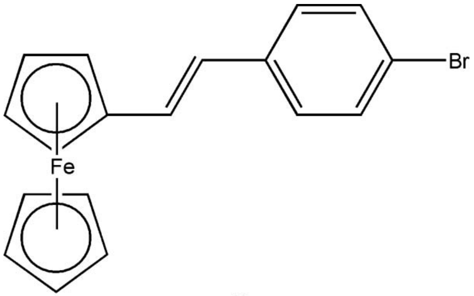
Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.008 Å
R factor = 0.035
wR factor = 0.089
Data-to-parameter ratio = 14.4

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

In the title compound, [Fe(C_5H_5)($C_{13}H_{10}$Br)], the benzene ring makes a dihedral angle of 14.1 (2)° with the substituted cyclopentadienyl ring. The bond distances imply that there is no conjugation between the cyclopentadienyl and benzene rings.

Comment

The chemistry of ferrocene has received much attention because of its applications in many fields, such as in catalysis (Yang *et al.*, 2002) and non-linear optical (NLO) materials (Long, 1995; Roberto *et al.*, 2000). As part of our continuing studies on non-linear optical materials, we present here the structure of the title compound, (I).



(I)

The molecular structure of (I) is shown in Fig. 1. The two cyclopentadienyl rings are nearly parallel [dihedral angle 0.9 (4)°] and exhibit an eclipsed conformation. The C1—C11 and C12—C13 bond distances (Table 1) are close to the typical single C—C bond distance of 1.48 Å for sp^2-hybridized C atoms, and the C11=C12 bond distance is identical to the typical C=C double-bond distance (Morrison *et al.*, 1973). This suggests that there is no conjugation between the cyclopentadienyl and benzene rings. The benzene ring makes a dihedral angle of 14.1 (2)° with the C1-containing cyclopentadienyl ring.

Experimental

For the preparation of (4-bromobenzyl)terphenylphosphonium bromide, a flask was charged with a mixture 1-bromo-4-methylbenzene (8.55 g, 50 mmol), NBS (*N*-bromosuccinimide) (9.2 g, 51 mmol) and a catalytic amount of benzoyl peroxide (BPO), which was vigorously stirred in tetrachloromethane (150 ml). The mixture was refluxed for 5 h. When the reaction was complete, it was cooled to room temperature and was extracted with chloroform several times. The organic layer was washed with water and saturated brine. The organic extracts were dried over $MgSO_4$. After removing the solvent under reduced pressure, the residue was collected and dried in a vacuum. This intermediate was added to triphenylphosphine (13.1 g, 50 mmol) in benzene (150 ml), and the resulting solution was refluxed for 4 h. After cooling to room temperature, a white solid was collected by filtration and air-dried to give 16.1 g (yield: 63%).

For the preparation of (*E*)-1-(4-bromobenzylidene)ferrocene, ferrocenealdehyde (3.2 g, 15 mmol), (4-bromobenzyl)terphenylphosphonium bromide (7.9 g, 15 mmol) and powdered NaOH (2.4 g, 60 mmol) were crushed together with a pestle and mortar for 2 h (Yang *et al.*, 2005). The mixture was extracted with dichloromethane three times. The organic layer was washed successively with water and saturated brine. The organic extracts were dried over $MgSO_4$. After removing the solvent under reduced pressure, the residue was purified by flash column chromatography and gave the product as a red solid. Single crystals of (I) were obtained by slow evaporation of a dichloromethane/2-propanol solution.

Crystal data

$[Fe(C_5H_5)(C_{13}H_{10}Br)]$
$M_r = 367.06$
Orthorhombic, $P2_12_12_1$
$a = 6.0159$ (14) Å
$b = 11.014$ (3) Å
$c = 22.347$ (5) Å
$V = 1480.7$ (6) Å^3
$Z = 4$
$D_x = 1.647$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2888 reflections
$\theta = 2.6$–23.8°
$\mu = 3.70$ mm^{-1}
$T = 273$ (2) K
Block, red
0.47 × 0.45 × 0.44 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.185$, $T_{max} = 0.196$
7751 measured reflections
2601 independent reflections
2219 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 25.0°$
$h = -7 \rightarrow 7$
$k = -13 \rightarrow 13$
$l = -19 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.089$
$S = 1.00$
2601 reflections
181 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}
Absolute structure: Flack (1983), 1064 Friedel Pairs
Flack parameter: −0.005 (17)

Table 1
Selected bond lengths (Å).

Br1—C16	1.901 (5)	C11—C12	1.317 (7)
C1—C11	1.466 (7)	C12—C13	1.452 (7)

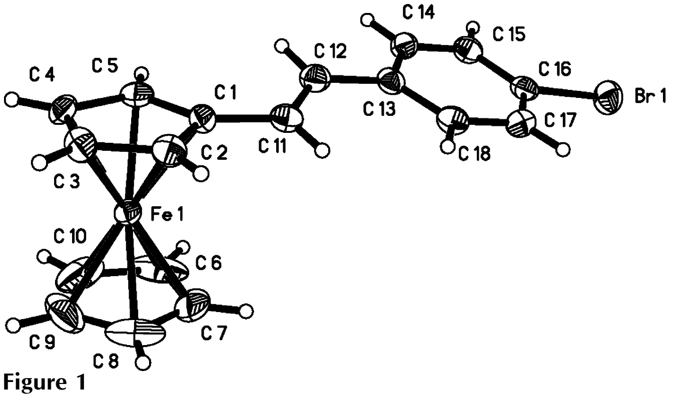


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids (arbitrary spheres for H atoms).

H atoms were placed in calculated positions (C—H = 0.93 Å) and refined in the riding mode [$U_{iso}(H) = 1.2U_{eq}(C)$].

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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