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Tetra-*n*-butylammonium ferrocenyltrifluoroborate

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Of the two independent ferrocenyltrifluoroborate anions in the asymmetric unit of the title compound, $(C_{16}H_{36}N)$-$[Fe(C_5H_5)(C_5H_4BF_3)]$, one has the BF_3 group nearly eclipsed and the other has the BF_3 group staggered, with respect to the plane of a cyclopentadienyl ring. The compound is the first structure determination of a ferrocenyltrifluoroborate anion.

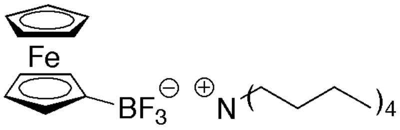
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.004 Å
R factor = 0.048
wR factor = 0.123
Data-to-parameter ratio = 21.2

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

Comment

In an attempt to synthesize organodifluoroboranes by treating the corresponding boronic acids with hydrofluoric acid (Kinder & Katzenellenbogen, 1985), it was discovered that the organodifluoroborane species would readily pick up a third fluoride anion to form the organotrifluoroborate species (confirmed by ^{11}B NMR). It was hypothesized that the species formed was the hydronium organotrifluoroborate salt; however, all attempts to isolate these compounds were unsuccessful, and they were observable only in solution *via* ^{11}B and ^{19}F NMR. Treatment of the intermediate with the base tetra-*n*-butylammonium hydroxide effected a counter-ion exchange to produce the organotrifluoroborate species with an organic counter-ion. These new compounds were found to have the same reactivity as their potassium organotrifluoroborate counterparts with the added bonus of increased solubility in organic media.



(I)

The title compound, (I), was synthesized to demonstrate the versatility of the counter-ion exchange reaction, and its tolerance for a variety of functional groups. The base used in the reaction can also be varied. Other examples generated in our group include sodium, potassium, caesium, and tetra-*n*-butylphosphonium counter-ions (Batey & Quach, 2001).

In space group $P\overline{1}$ with Z = 4, the asymmetric unit must contain two molecules. In the asymmetric unit of (I), there are two ionic pairs (A and B in Fig. 1); each pair consists of a ferrocenyltrifluoroborate anion and a tetra-*n*-butylammonium cation and the anions have different conformations. In anion A, the BF_3 group is almost eclipsed to the bonded cyclopentadienyl ring [defined by the torsion angle C2A—C1A—B1A—F2A of −5.5 (4)°] and in anion B, the BF_3 group is

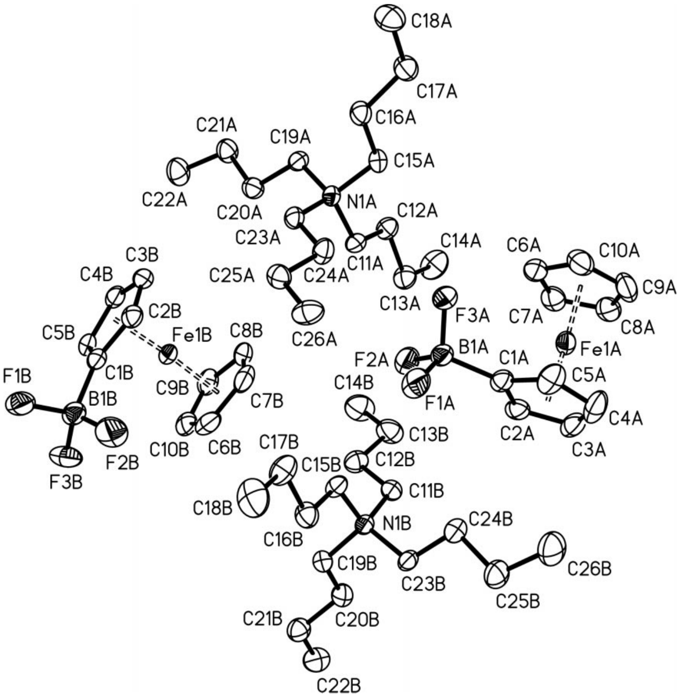


Figure 1

View of (I) showing the atom-labelling scheme. Ellipsoids are at the 50% probability level.

staggered with respect to the bonded cyclopentadienyl ring [defined by the torsion angle C2*B*—C1*B*—B1*B*—F1*B* of 90.5 (3)°]. See Table 1 for other torsion angles relating to the BF_3 geometry.

A search of the April 2001 release of the Cambridge Structural Database (Allen & Kennard, 1993) revealed that this is the first structure determination of a ferrocenyltrifluoroborate anion.

Experimental

Compound (I) was synthesized by treatment of ferroceneboronic acid (0.52 g, 4.27 mmol), dissolved in a minimum amount of methanol (*ca* 1 ml), with a 5.0 *M* solution of hydrofluoric acid (2.65 ml, 13.25 mmol), added dropwise with vigorous stirring over a period of 1 min at room temperature. The reaction mixture was then cooled to 273 K, and a 1.54 *M* solution of tetra-*n*-butylammonium hydroxide (2.76 ml, 4.27 mmol) was added dropwise over a period of 5 min. The reaction mixture was then warmed to room temperature and stirred for another hour. Dichloromethane (10 ml) was added to dilute the biphasic reaction mixture, the layers were separated, and the aqueous layer was further extracted with dichloromethane (3 × 10 ml). The combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo* to afford the dark green crystalline solid (I). Subsequent recrystallization in ethyl acetate and hexanes yielded the desired crystals.

Crystal data

$(C_{16}H_{36}N)[Fe(C_5H_5)(C_5H_4BF_3)]$
$M_r = 495.29$
Triclinic, $P\overline{1}$
$a = 9.9310\ (2)$ Å
$b = 15.5450\ (4)$ Å
$c = 17.9230\ (5)$ Å
$\alpha = 87.4990\ (14)°$
$\beta = 87.9350\ (17)°$
$\gamma = 75.3340\ (16)°$
$V = 2673.31\ (11)$ Å^3
$Z = 4$
$D_x = 1.231$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 33 767 reflections
$\theta = 2.6–27.5°$
$\mu = 0.60$ mm^{-1}
$T = 150\ (1)$ K
Needle, orange
0.25 × 0.15 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.865$, $T_{\max} = 0.916$
50 155 measured reflections
12 237 independent reflections
8213 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 27.5°$
$h = -12 \rightarrow 12$
$k = -19 \rightarrow 20$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.123$
$S = 1.02$
12 237 reflections
578 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.1936P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.45$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

C1*A*—B1*A*	1.608 (3)	C1*B*—B1*B*	1.605 (4)
C5*A*—C1*A*—B1*A*	126.7 (2)	C5*B*—C1*B*—B1*B*	127.0 (2)
C2*A*—C1*A*—B1*A*	128.0 (2)	C2*B*—C1*B*—B1*B*	127.4 (2)
C2*A*—C1*A*—B1*A*—F1*A*	113.5 (3)	C2*B*—C1*B*—B1*B*—F1*B*	90.5 (3)
C2*A*—C1*A*—B1*A*—F2*A*	−5.5 (4)	C2*B*—C1*B*—B1*B*—F2*B*	−27.9 (3)
C2*A*—C1*A*—B1*A*—F3*A*	−126.3 (3)	C2*B*—C1*B*—B1*B*—F3*B*	−150.0 (2)

H atoms were included in calculated positions with C—H distances ranging from 0.98 to 1.00 Å.

Data collection: *COLLECT* (Nonius, 1997–2001); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1999); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

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