Crystal structure of pentafluorophenyl ferrocene, $Fe(C_5H_5)(C_{11}H_4F_5)$

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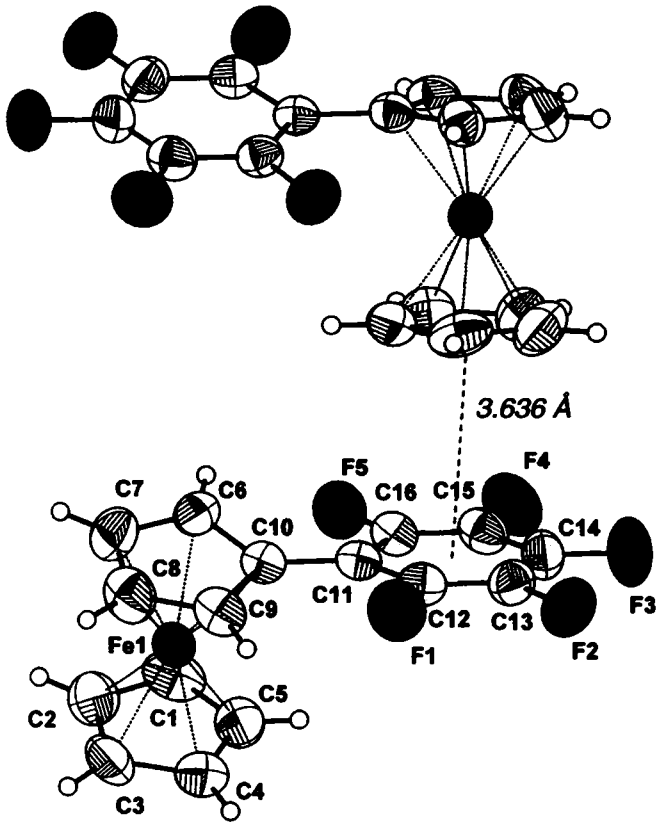

Abstract

$C_{16}H_9F_5Fe$, orthorhombic, *Fdd2* (no. 43), $a = 19.6794(5)$ Å, $b = 20.7759(6)$ Å, $c = 12.6899(3)$ Å, $V = 5188.4$ Å^3, $Z = 16$, $R_{gt}(F) = 0.042$, $wR_{ref}(F^2) = 0.095$, $T = 293$ K.

Source of material

The title compound was prepared by a modified procedure according to [1]. A mixture of ferrocene (250 mg, 1.34 mmol) in dry diethylether (20 mL) was stirred for 2 hours at room temperature under argon atmosphere. A 1.55 M solution of *tert*-butyl lithium (1.8 mL, 1.34 mmol) in hexane and tetramethylethylenediamine (156 mg, 1.34 mmol) were subsequently added under continuous stirring. The resulting viscous reaction mixture was diluted with dry tetrahydrofurane (10 mL). After the addition of hexafluorobenzene (395 mg, 1.34 mmol) at –78 °C the reaction mixture was stirred for 24 hours at room temperature. The synthesis of the title compound yielded in a complex mixture of ferrocene derivatives. Analyzing the chromatography fractions by chemical ionization mass spectroscopy (NH_3) the various side products can be detected. The following molecular formulas are attributed to the observed mass peaks (*m/z*): (a) title compound FcC_6F_4: 353.0042 ($C_{16}H_{10}F_5Fe$, M+H), (b) $C_6F_5FcC_6F_5$: 519.0113 ($C_{26}H_{19}F_4Fe_2$; M+H), (c) FcC_6F_4-Fc-C_6F_5: 684.9940 ($C_{32}H_{18}F_9Fe_2$, M+H), (d) $C_6F_5FcC_6F_4FcC_6F_5$: 850.9792 ($C_{38}H_{17}F_{14}Fe_2$, M+H). Pure pentafluorophenyl-ferrocene was isolated by fractional crystallization. The solvents were evaporated and the residue was chromatographed over silica gel eluting with 20 % dichloromethane in cyclohexane. The third fraction was collected and fractional crystallization from chloroform afforded single crystals of the title compound.

Discussion

In the crystal structure of pentafluorophenyl-ferrocene, the two cyclopentadienyl (Cp) cycles of the ferrocene are in an eclipsed conformation. The molecule displays a torsion angle between the phenyl and the Cp planes of 21.27°, probably due to the interactions between the *ortho* fluorine and the *ortho* hydrogen atoms. The respective interactions can be interpreted as intramolecular hydrogen bonds ($d_{H\cdots F}$ = 2.357 Å and 2.372 Å, ∠C–H···F = 110.1° and 110.0°). The interplay of H···F and π–π interactions is responsible for the observed crystal structure. The numerous H···F contacts between the non-substituted Cp and the pentafluorophenyl rings vary from $d_{H\cdots F}$ = 2.66 Å to 2.82 Å forming cross-linked two-dimensional networks since one of two molecules is oriented upside down. In the third dimension, there are significant intermolecular π–π stacking interactions, in which again the non-substituted Cp fragments of the ferrocene and the pentafluorophenyl groups are partially engaged with a centroid-centroid distance of 3.636(2) Å. The crystal is a non-racemic twin with a ratio of 0.38(2)/0.62 (refined twin parameter).The crystal structure of the non-fluorinated phenyl-ferrocene was reported in [2].

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.36 × 0.38 × 0.45 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	12.14 cm^{-1}
Diffractometer, scan mode:	Nonius KappaCCD, φ/ω
$2\theta_{max}$:	66.24°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	18561, 4650
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2911
$N(param)_{refined}$:	201
Programs:	SHELXS-97 [3], SHELXL-97 [4], DIAMOND [5]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	16*b*	0.3352	0.0718	0.0549	0.081
H(2)	16*b*	0.3058	0.1879	0.0353	0.091
H(3)	16*b*	0.1844	0.1950	–0.0208	0.081
H(4)	16*b*	0.1382	0.0825	–0.0332	0.070
H(5)	16*b*	0.2322	0.0076	0.0123	0.070
H(6)	16*b*	0.2906	0.0744	0.3033	0.062
H(7)	16*b*	0.2620	0.1923	0.2885	0.081
H(8)	16*b*	0.1400	0.2012	0.2339	0.081
H(9)	16*b*	0.0918	0.0912	0.2178	0.064

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	16*b*	0.21631(2)	0.11196(2)	0.13507(4)	0.0459(2)	0.0408(2)	0.0477(2)	0.0033(2)	0.0007(2)	0.0023(2)
C(1)	16*b*	0.2932(2)	0.0882(2)	0.0351(3)	0.051(2)	0.095(3)	0.057(2)	0.012(2)	0.010(2)	0.014(2)
C(2)	16*b*	0.2767(2)	0.1533(2)	0.0240(4)	0.082(3)	0.080(3)	0.067(2)	–0.029(2)	0.001(2)	0.015(2)
C(3)	16*b*	0.2084(2)	0.1573(2)	–0.0073(3)	0.091(3)	0.052(2)	0.059(2)	0.005(2)	–0.003(2)	0.017(2)
C(4)	16*b*	0.1823(2)	0.0940(2)	–0.0147(3)	0.055(2)	0.069(2)	0.052(2)	0.003(2)	–0.004(2)	0.003(2)
C(5)	16*b*	0.2351(2)	0.0522(2)	0.0112(3)	0.068(2)	0.056(2)	0.050(2)	0.004(2)	0.009(2)	–0.004(1)
C(6)	16*b*	0.2486(2)	0.0915(2)	0.2846(2)	0.056(2)	0.051(2)	0.049(2)	–0.002(1)	–0.007(1)	–0.005(1)
C(7)	16*b*	0.2325(2)	0.1581(2)	0.2762(3)	0.082(3)	0.053(2)	0.066(2)	–0.005(2)	–0.003(2)	–0.013(2)
C(8)	16*b*	0.1635(2)	0.1630(2)	0.2457(3)	0.088(3)	0.047(2)	0.067(2)	0.022(2)	0.009(2)	–0.005(2)
C(9)	16*b*	0.1364(2)	0.1010(2)	0.2361(3)	0.049(2)	0.058(2)	0.053(2)	0.017(1)	0.009(1)	0.002(1)
C(10)	16*b*	0.1885(1)	0.0551(1)	0.2591(2)	0.041(1)	0.045(1)	0.041(1)	0.006(1)	0.004(1)	–0.001(1)
C(11)	16*b*	0.1821(1)	–0.0153(1)	0.2583(2)	0.039(1)	0.047(1)	0.036(1)	0.005(1)	0.000(1)	0.001(1)
C(12)	16*b*	0.1202(1)	–0.0469(2)	0.2679(2)	0.039(1)	0.056(2)	0.047(2)	0.004(1)	0.000(1)	0.001(1)
C(13)	16*b*	0.1135(2)	–0.1127(2)	0.2676(3)	0.058(2)	0.058(2)	0.047(2)	–0.014(1)	0.001(1)	0.001(1)
C(14)	16*b*	0.1698(2)	–0.1510(2)	0.2595(3)	0.080(2)	0.041(2)	0.052(2)	–0.005(1)	0.003(2)	0.001(1)
C(15)	16*b*	0.2320(2)	–0.1224(2)	0.2491(3)	0.060(2)	0.050(2)	0.048(2)	0.016(1)	0.002(1)	0.002(1)
C(16)	16*b*	0.2379(1)	–0.0568(1)	0.2486(2)	0.042(1)	0.049(2)	0.044(1)	0.005(1)	0.003(1)	0.003(1)
F(1)	16*b*	0.06324(9)	–0.0126(1)	0.2781(2)	0.0364(9)	0.079(1)	0.096(2)	0.0057(8)	0.0057(9)	0.007(1)
F(2)	16*b*	0.0516(1)	–0.1393(1)	0.2767(2)	0.070(1)	0.086(2)	0.079(1)	–0.034(1)	0.004(1)	–0.000(1)
F(3)	16*b*	0.1637(1)	–0.2149(1)	0.2606(2)	0.133(2)	0.044(1)	0.095(2)	–0.010(1)	0.016(2)	–0.002(1)
F(4)	16*b*	0.2882(1)	–0.1590(1)	0.2397(2)	0.083(1)	0.063(1)	0.086(2)	0.034(1)	0.014(1)	0.007(1)
F(5)	16*b*	0.30086(8)	–0.03204(9)	0.2375(2)	0.0366(8)	0.064(1)	0.084(1)	0.0062(7)	0.0062(8)	0.006(1)

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