Crystal structure of pentaphenylferrocenium tetrafluoroborate, $C_{40}H_{30}BF_4Fe$

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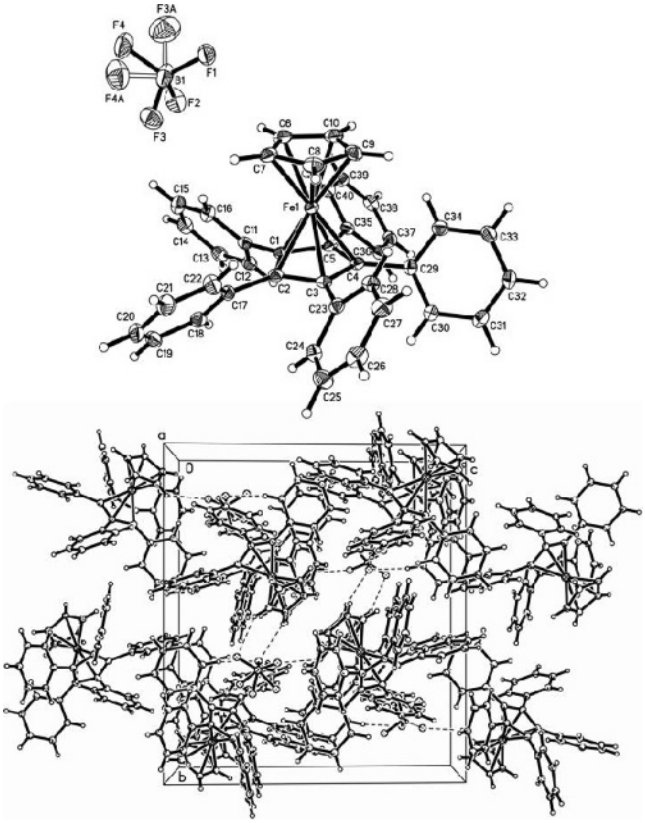

Abstract

$C_{40}H_{30}BF_4Fe$, monoclinic, $P2_1/n$ (no. 14), a = 9.8978(6) Å, b = 18.7154(10) Å, c = 16.7027(10) Å, β = 94.144(4)°, V = 3085.9(3) Å^3, Z = 4, $R_{gt}(F)$ = 0.0452, $wR_{ref}(F^2)$ = 0.1185, T = 100 K.

Table 1. Data collection and handling.

Crystal:	dark-yellow plates, size 0.07×0.12×0.25 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	43.62 cm^{-1}
Diffractometer, scan mode:	Bruker Kappa APEX II Duo, ω and φ
$2\theta_{max}$:	132.8°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	17588, 5231
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4189
$N(param)_{refined}$:	434
Programs:	SHELX [8]

Source of material

Paramagnetic pentaphenylferrocene based palladacycle complexes [1] were previously reported to be the most efficient catalysts for the asymmetric rearrangement of allylic imidates in terms of catalytic activity and enantioselectivity [2,3]. Oxidation of the diamagnetic precatalysts to the paramagnetic active species was found to be indispensable for high catalytic activity [4]. Spectroscopic and mechanistic evidence has suggested that the activated species is in agreement with an Fe(II)/Pd(III) resonance structure, in which Pd(III) acts as Lewis acid with largly enhanced activity as compared to Pd(II) complexes. For the purpose of comparison with the activated catalyst [1] we investigated the structure of the parent pentaphenylferrocenium reference system. Pentaphenylferrocene (17.5mg) was dissolved in dry dichlorommethane (DCM) and added to $AgBF_4$ (6.0mg, 1 equiv.) under N_2. The reaction was stirred for 24 h at room temperature. The suspension was filtrated under nitrogen over celite. The solvent was removed by a constant stream of N_2 to give brown pentaphenyl-ferrocenium tetrafluoroborate (20.3 mg, quant.) followed by recrystallization from DCM at room temperature yielding in dark-yellow crystal plates of the title compound, m.p. > 300°C (decomp.).

Experimental details

H atoms were located on difference fourier maps, but refined with fixed individual displacement parameters, using a riding model with d(C–H) distances of 0.95 Å. The population parameters of the disordered fluorines of the anion were refined free with weak support of constraints for better convergence of the refinement.

Discussion

The title compound (figure, top) crystallizes with one independent ion pair in the asymmetric unit of the space group $P2_1/n$. The center distance of the Cp-rings is 3.44 Å which is equivalent observed in the activated catalyst (3.46 Å) [1] (see: Source of material) and in contrast to the unusually large distance (3.58 Å) reported in the decaphenyl-ferrocenium tetrafluoroborate [5,6].
The orientation of the Cp-rings is nearly parallel. The interplanar angle is 2.6(2)°. The activated catalyst [1] species shows a larger deviation with 11.7(6)° and 8.4(4)°.
The Cp-rings are also screwed out of the face-to-face orientation characterized by an average torsionangle (Cp1–Cp2) of 9°. The π-bond distances of the Cp-ring where the phenyl moieties are attached, shows an average elongation of 2.1(4) pm in relation to the hydrogen substituted Cp-ring.
The interplanar angles between the Cp-ring and the attached phenyl moieties are in an intervall of 47° to 57° which is an expected behaviour.
The cell plot (figure, bottom) shows a couple of electrostatic interactions between π-systems as donors and the fluor atoms as acceptors. Two fluorines were fixed by two interactions: The H26···F1 distance is 2.41 Å and the H9···F1 distance is 2.44 Å and the corresponding angles C26–H26···F1 and C9–H9···F1 are 146° and 125°, respectively. The H30···F2 and H6···F2 distances are

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2.44 Å and 2.54 Å with related angles C30–H30···F2 and C6–H6···F2 of
F3A is 2.56 Å and the corresponding angle
C38–H38···F3A is also 145°.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(6)	4*e*	0.2801	–0.0296	0.8892	0.028
H(7)	4*e*	0.4696	–0.0083	0.7973	0.028
H(8)	4*e*	0.6142	0.0936	0.8558	0.027
H(9)	4*e*	0.5155	0.1344	0.9835	0.026
H(10)	4*e*	0.3086	0.0586	1.0041	0.028
H(12)	4*e*	–0.1045	0.1490	0.7562	0.024
H(13)	4*e*	–0.2809	0.0705	0.7195	0.028
H(14)	4*e*	–0.2373	–0.0508	0.6994	0.031
H(15)	4*e*	–0.0140	–0.0921	0.7086	0.031
H(16)	4*e*	0.1645	–0.0132	0.7425	0.026
H(18)	4*e*	0.1045	0.1335	0.6077	0.024
H(19)	4*e*	0.1468	0.0964	0.4782	0.031
H(20)	4*e*	0.3653	0.0647	0.4488	0.033
H(21)	4*e*	0.5423	0.0689	0.5494	0.035
H(22)	4*e*	0.5001	0.1030	0.6791	0.031
H(24)	4*e*	0.3852	0.2648	0.6456	0.024
H(25)	4*e*	0.5798	0.3191	0.6029	0.030
H(26)	4*e*	0.7740	0.3287	0.6898	0.030
H(27)	4*e*	0.7717	0.2874	0.8219	0.030
H(28)	4*e*	0.5773	0.2339	0.8662	0.025
H(30)	4*e*	0.2900	0.3549	0.8296	0.025
H(31)	4*e*	0.3205	0.4494	0.9206	0.030
H(32)	4*e*	0.3503	0.4264	1.0577	0.028
H(33)	4*e*	0.3465	0.3089	1.1049	0.028
H(34)	4*e*	0.3127	0.2146	1.0152	0.024
H(36)	4*e*	0.0119	0.2731	0.9130	0.021
H(37)	4*e*	–0.1725	0.2664	0.9922	0.027
H(38)	4*e*	–0.2497	0.1558	1.0353	0.026
H(39)	4*e*	–0.1361	0.0512	1.0012	0.028
H(40)	4*e*	0.0471	0.0570	0.9218	0.025

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	4*e*		0.33631(5)	0.11112(2)	0.85298(3)	0.0178(2)	0.0142(2)	0.0164(2)	0.0013(2)	0.0012(2)	0.0008(2)
C(1)	4*e*		0.1558(3)	0.1271(1)	0.7799(2)	0.017(2)	0.015(1)	0.017(1)	0.003(1)	–0.001(1)	0.002(1)
C(2)	4*e*		0.2686(3)	0.1489(1)	0.7372(2)	0.017(1)	0.016(1)	0.017(2)	0.005(1)	–0.000(1)	0.002(1)
C(3)	4*e*		0.3400(3)	0.2046(1)	0.7829(2)	0.019(2)	0.015(1)	0.016(1)	0.002(1)	–0.001(1)	0.003(1)
C(4)	4*e*		0.2682(3)	0.2174(1)	0.8536(2)	0.016(1)	0.013(1)	0.016(1)	0.002(1)	0.002(1)	0.002(1)
C(5)	4*e*		0.1557(3)	0.1692(1)	0.8523(2)	0.020(2)	0.011(1)	0.017(1)	0.002(1)	0.002(1)	0.002(1)
C(6)	4*e*		0.3495(3)	0.0054(2)	0.8967(2)	0.027(2)	0.019(1)	0.024(2)	0.005(1)	0.003(1)	0.007(1)
C(7)	4*e*		0.4555(3)	0.0173(2)	0.8451(2)	0.030(2)	0.017(1)	0.024(2)	0.007(1)	0.003(1)	0.003(1)
C(8)	4*e*		0.5364(3)	0.0742(2)	0.8780(2)	0.016(2)	0.025(2)	0.026(2)	0.006(1)	0.003(1)	0.007(1)
C(9)	4*e*		0.4811(3)	0.0971(2)	0.9493(2)	0.019(2)	0.026(2)	0.020(2)	0.002(1)	–0.005(1)	0.003(1)
C(10)	4*e*		0.3654(3)	0.0546(2)	0.9608(2)	0.026(2)	0.020(2)	0.023(2)	0.007(1)	0.002(1)	0.007(1)
C(11)	4*e*		0.0477(3)	0.0754(2)	0.7542(2)	0.020(2)	0.017(1)	0.013(1)	–0.002(1)	0.003(1)	0.002(1)
C(12)	4*e*		–0.0856(3)	0.1001(2)	0.7467(2)	0.021(2)	0.021(1)	0.017(2)	0.001(1)	0.001(1)	0.001(1)
C(13)	4*e*		–0.1904(3)	0.0533(2)	0.7253(2)	0.019(2)	0.031(2)	0.020(2)	–0.000(1)	–0.001(1)	0.002(1)
C(14)	4*e*		–0.1647(3)	–0.0187(2)	0.7124(2)	0.025(2)	0.029(2)	0.022(2)	–0.010(1)	0.002(1)	–0.001(1)
C(15)	4*e*		–0.0324(3)	–0.0431(2)	0.7184(2)	0.028(2)	0.022(2)	0.028(2)	–0.004(1)	0.005(1)	–0.006(1)
C(16)	4*e*		0.0739(3)	0.0038(2)	0.7389(2)	0.021(2)	0.019(2)	0.025(2)	–0.002(1)	0.005(1)	–0.004(1)
C(17)	4*e*		0.2981(3)	0.1221(1)	0.6563(2)	0.022(2)	0.016(1)	0.014(1)	–0.003(1)	0.005(1)	–0.001(1)
C(18)	4*e*		0.1935(3)	0.1200(2)	0.5961(2)	0.022(2)	0.018(1)	0.021(2)	–0.002(1)	0.004(1)	0.002(1)
C(19)	4*e*		0.2188(3)	0.0982(2)	0.5190(2)	0.037(2)	0.024(2)	0.016(2)	–0.008(1)	0.001(1)	0.002(1)
C(20)	4*e*		0.3480(3)	0.0793(2)	0.5016(2)	0.042(2)	0.022(2)	0.020(2)	–0.003(1)	0.009(1)	–0.004(1)
C(21)	4*e*		0.4531(4)	0.0816(2)	0.5615(2)	0.032(2)	0.027(2)	0.028(2)	0.009(1)	0.011(2)	–0.004(1)
C(22)	4*e*		0.4282(3)	0.1023(2)	0.6383(2)	0.023(2)	0.030(2)	0.023(2)	0.004(1)	0.000(1)	–0.002(1)
C(23)	4*e*		0.4627(3)	0.2421(1)	0.7596(2)	0.019(2)	0.015(1)	0.020(2)	0.002(1)	0.004(1)	–0.001(1)
C(24)	4*e*		0.4638(3)	0.2688(2)	0.6815(2)	0.021(2)	0.022(2)	0.018(2)	–0.000(1)	0.002(1)	–0.003(1)
C(25)	4*e*		0.5796(3)	0.3012(2)	0.6561(2)	0.025(2)	0.030(2)	0.020(2)	–0.003(1)	0.005(1)	0.002(1)
C(26)	4*e*		0.6944(3)	0.3074(2)	0.7077(2)	0.018(2)	0.026(2)	0.033(2)	–0.003(1)	0.008(1)	0.001(1)
C(27)	4*e*		0.6932(3)	0.2824(2)	0.7861(2)	0.018(2)	0.024(2)	0.032(2)	0.002(1)	–0.005(1)	0.002(1)
C(28)	4*e*		0.5779(3)	0.2503(2)	0.8124(2)	0.022(2)	0.019(1)	0.020(2)	0.002(1)	–0.001(1)	0.003(1)
C(29)	4*e*		0.2978(3)	0.2749(2)	0.9134(2)	0.016(1)	0.018(1)	0.017(2)	–0.002(1)	0.003(1)	–0.003(1)
C(30)	4*e*		0.3008(3)	0.3455(2)	0.8856(2)	0.024(2)	0.018(1)	0.019(2)	–0.001(1)	–0.000(1)	–0.001(1)
C(31)	4*e*		0.3196(3)	0.4016(2)	0.9396(2)	0.029(2)	0.017(1)	0.029(2)	–0.001(1)	0.003(1)	–0.002(1)
C(32)	4*e*		0.3368(3)	0.3880(2)	1.0209(2)	0.025(2)	0.021(2)	0.023(2)	–0.004(1)	0.003(1)	–0.008(1)
C(33)	4*e*		0.3345(3)	0.3181(2)	1.0489(2)	0.027(2)	0.027(2)	0.017(2)	–0.002(1)	0.000(1)	–0.001(1)
C(34)	4*e*		0.3148(3)	0.2622(2)	0.9956(2)	0.022(2)	0.020(1)	0.020(2)	0.000(1)	0.002(1)	0.002(1)
C(35)	4*e*		0.0481(3)	0.1657(2)	0.9093(2)	0.016(1)	0.017(1)	0.014(1)	–0.001(1)	0.001(1)	0.002(1)
C(36)	4*e*		–0.0182(3)	0.2279(2)	0.9307(2)	0.019(2)	0.018(1)	0.017(1)	0.002(1)	0.001(1)	–0.002(1)
C(37)	4*e*		–0.1281(3)	0.2238(2)	0.9777(2)	0.023(2)	0.025(2)	0.018(2)	0.007(1)	–0.001(1)	–0.003(1)
C(38)	4*e*		–0.1737(3)	0.1583(2)	1.0038(2)	0.015(2)	0.033(2)	0.018(2)	–0.003(1)	0.003(1)	–0.000(1)
C(39)	4*e*		–0.1065(3)	0.0963(2)	0.9830(2)	0.025(2)	0.025(2)	0.021(2)	–0.007(1)	0.003(1)	0.003(1)
C(40)	4*e*		0.0027(3)	0.0996(2)	0.9360(2)	0.025(2)	0.018(1)	0.020(2)	0.000(1)	0.001(1)	–0.000(1)
B(1)	4*e*		0.4420(4)	–0.1665(2)	0.8088(3)	0.030(2)	0.031(2)	0.047(3)	0.008(2)	–0.012(2)	–0.018(2)
F(1)	4*e*		0.5217(2)	–0.1439(1)	0.8740(1)	0.032(1)	0.033(1)	0.028(1)	0.0058(8)	–0.0050(8)	–0.0081(8)
F(2)	4*e*		0.3123(2)	–0.1421(1)	0.8080(1)	0.025(1)	0.053(1)	0.034(1)	0.0020(9)	0.0015(8)	–0.008(1)

Table 3. continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
F(3)	4*e*	0.788	0.4991(3)	–0.1269(1)	0.7403(1)	0.034(2)	0.043(2)	0.027(1)	0.002(1)	0.007(1)	0.003(1)
F(4)	4*e*	0.788	0.4592(3)	–0.2364(2)	0.7905(2)	0.045(2)	0.029(2)	0.047(2)	–0.002(1)	–0.004(2)	–0.016(1)
F(3A)	4*e*	0.212	0.391(1)	–0.2248(6)	0.8676(7)	0.055(6)	0.059(6)	0.082(7)	0.011(5)	–0.007(5)	0.005(5)
F(4A)	4*e*	0.212	0.474(1)	–0.2074(8)	0.7497(7)	0.051(6)	0.064(6)	0.046(6)	0.005(5)	0.007(5)	–0.015(5)

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