The synthesis and structure of ferrocenylalkyl onium derivatives of nitrogen-containing heterocyclic compounds

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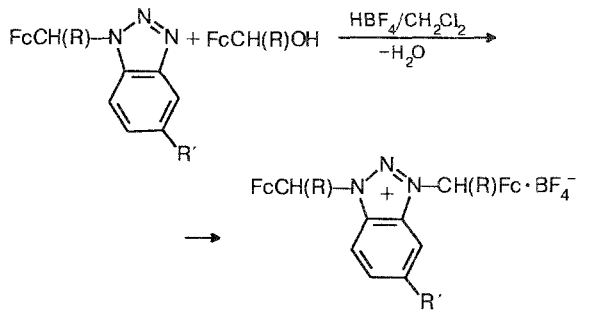
The reactions of hydroxymethylferrocene, α-hydroxyethylferrocene, and 1,1′-bis(α-hydroxyethyl)ferrocene with *N*-ferrocenylalkyl-substituted benzotriazoles, hexamethylenetetramine, and azaferrocene in the CH_2Cl_2 — 48% aqueous HBF_4 two-phase system afforded *N*-mono-, *N*-1,1′-ferrocenylene-bis-α-alkylated, and 1,3-bis-ferrocenylalkylated tetrafluoroborates of the above-mentioned heterocyclic compounds in high yields. An X-ray structural study of 1,3-bis-(ferrocenylmethyl)benzotriazolium tetrafluoroborate confirmed unambiguously the 1,3-arrangement of the ferrocenylmethyl groups in the heterocycle.

Key words: ferrocenylalkylation, derivatives of nitrogen-containing heterocyclic compounds, X-ray diffraction analysis, NMR spectra.

The reactions of ferrocenylalkylation[1,2] allow one to prepare a variety of ferrocene derivatives that possess biological activity.[3,4] Various methods for conducting these reactions exist.[2,5—9] In our opinion, ferrocenylalkylation carried out as the interaction of equimolar amounts of α-hydroxyalkylferrocenes with nucleophiles (Nu) in a two-phase system consisting of a polar organic solvent (CH_2Cl_2, $C_2H_4Cl_2$, or $CHCl_3$) and a 40—70% aqueous solution of an acid, HX (X = BF_4, ClO_4) is the most convenient and general of these methods.[2] Both neutral type $FcC(RR^1)Nu$[10,11] ferrocene derivatives and $[FcC(RR^1)Nu^+]X^-$ salts (Fc = $C_5H_5FeC_5H_4$)[12—14] were prepared by this method in high yields. In the present work we synthesized novel types of mono-, 1,1-ferrocenylene-bis-α-alkyl, and 1,3-bis(ferrocenylalkyl) onium derivatives of nitrogen-containing heterocyclic compounds and studied their structures.



1: R = H, R′ = H,
2: R = H, R′ = Me,
3: R = H, R′ = Br,
4: R = H, R′ = NO_2,
5: R = Me, R′ = H.

1—5

Results and Discussion

The interaction of equimolar amounts of hydroxymethylferrocene or α-hydroxyethylferrocene with *N*-ferrocenylalkyl-substituted benzotriazole[11] in the CH_2Cl_2 — 48 % aqueous HBF_4 two-phase system gave 1,3-bis(ferrocenylalkyl)benzotriazolium tetrafluoroborates (**1—5**) in almost quantitative yields.

The quaternization occurs at ambient temperature over a period of 5—8 min, and the salts **1—5** that form require no additional purification, since when they are isolated they are analytically pure. Under similar conditions, 1,1′-di(α-hydroxyethyl)ferrocene smoothly reacted with 1-ferrocenylmethylbenzotriazole or hexamethylenetetramine at a molar ratio of reactants of 1 : 2 to yield products of 1,1′-ferrocenylene-bis-α-alkylation (**6**, **7**).

No dehydration or polymerization products, whose formation is possible in the absence of nucleophiles, were detected.[1]

N-α-ferrocenylalkylation of azaferrocene through the action of an equimolar amount of α-hydroxyethylfer-

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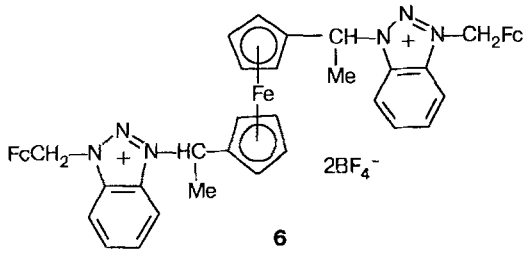
Table 1. Characteristics of compounds **1—8** synthesized

Compound	Yield (%)	M.p.* °C	Found / Calculated (%) C	H	F	Fe	N	Molecular formula	IR spectrum (KBr pellets) ν/cm^{-1}
1	96	105—107	52.97 52.62	4.38 4.73	11.71 11.89	17.37 17.48	6.71 6.57	$C_{28}H_{26}BF_4Fe_2N_3 \cdot 2H_2O$	3100, 1656, 1614, 1452, 1108, 1100—1020, 1006, 819
2	94	103—105	56.20 56.45	4.18 4.57		17.84 18.10	6.32 6.81	$C_{29}H_{28}BF_4Fe_2N_3$	3100, 3016, 2972, 2931, 2871, 1628, 1604, 1446, 1110, 1104—1015, 1007; 818
3	94	108	50.10 49.33	3.79 3.69			7.69 6.16	$C_{28}H_{25}BBrF_4Fe_2N_3$	3110, 3003, 1660, 1604, 1449, 1107, 1100—1013, 1003, 822
4	95	103—104	49.01 49.16	3.98 4.27	10.70 11.11	15.77 16.33	8.35 8.19	$C_{28}H_{25}BF_4Fe_2N_4O_2 \cdot H_2O$	3108, 3004, 1659, 1631, 1550, 1447, 1354, 1108, 1100—1012, 1003, 811
5	94	117—119	56.38 57.10	4.57 4.79		17.36 17.70		$C_{30}H_{30}BF_4Fe_2N_3$	3109, 3000, 2950, 1635, 1607, 1470, 1110, 1100—1021, 1007, 820
6	92	112—114	54.87 55.01	4.12 4.42	14.28 14.50	15.69 15.99	7.84 8.02	$C_{48}H_{46}B_2F_8Fe_3N_6$	3112, 3003, 2958, 1658, 1480, 1112, 1100—1020, 1005, 822
7	94	108	44.55 44.99	6.61 5.81	21.96 21.90		15.29 15.99	$C_{26}H_{40}B_2F_8FeN_8$	3310, 1712, 1471, 1412, 1310, 1272, 1235, 1103, 1012, 869, 828, 780
8	93		51.92 51.80	4.55 4.55		23.31 22.94	2.71 2.88)	$C_{21}H_{22}BF_4Fe_2N$	3650, 3572, 3500—3300, 3140, 2938, 2858, 1640, 1386, 1191, 1100—1015, 849

* With decomposition.



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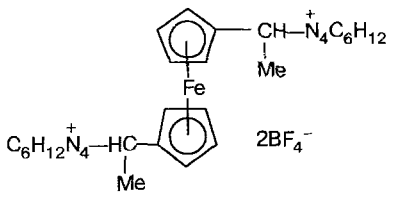

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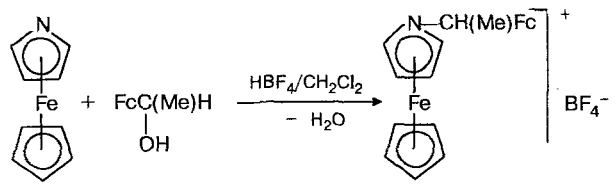
rocene gives *N*-(α-ferrocenylethyl)azoniaferrocene tetrafluoroborate **8** in a 93 % yield and no side products (Scheme 1).

Scheme 1



8

Salts **1—8** obtained are yellow or orange-colored crystalline compounds, stable when stored in air, readily

Table 2. The ^{1}H NMR chemical shifts ($(CD_3)_2CO$), δ for compounds **1**, **4**, **5**, **7**, and **8**

Compound	C_5H_5	C_5H_4	C_6H_4, C_6H_3	CH_2, CH, CH_3
1	4.27 (s, 14 H)	4.57 (t, 4 H)	7.93 (q, 2 H) 8.45 (q, 2 H)	6.14 (s, 4 H)
4	4.20—4.30 (m, 18 H)		8.71 (m, 2 H) 9.38 (s, 1 H)	6.25 (s, 2 H) 6.34 (s, 2 H)
5	4.15 (s, 6 H)	4.25—4.60 (m, 12 H)	8.00 (m, 2 H) 8.38 (m, 2 H)	6.64 (m, 2H) 2.25 (s, 3 H) 2.28 (s, 3 H)
7*	4.22-5.00 (m, 34 H)			4.03 (q, 2 H) 1.73 (6 H)
8**	4.40 s 4.55 s 4.61 s (10 H)	5.03 s 5.22 s (5 H)		2.14 (s, 3 H) 5.68 (s, 2 H, β-pyrrole) 6.70 (s, 2 H, α-pyrrole)

* Recorded in DMSO-d_6

** All of the signals of the protons of compound **8** are broadened (the width of the signals at the half-height is 9 Hz); the ^{11}B signal is located in the high field: δ = −18.94 (methyl borate was used as the external standard).

Table 3. The bond lengths (d/Å) in cations **A** and **B**

Bond	A	B	Bond	A	B	Bond	A	B
Fe(1)—C(11)	2.033(7)	2.021(6)	C(12)—C(13)	1.430(1)	1.410(1)	Fe(2)—C(30)	2.052(7)	2.032(9)
Fe(1)—C(12)	2.044(7)	2.024(7)	C(13)—C(14)	1.380(1)	1.430(1)	N(2)—N(3)	1.310(8)	1.301(8)
Fe(1)—C(13)	2.030(8)	2.045(7)	C(14)—C(15)	1.400(1)	1.400(1)	N(3)—C(6)	1.364(8)	1.387(9)
Fe(1)—C(14)	2.026(9)	2.059(7)	C(15)—C(11)	1.420(1)	1.410(1)	N(3)—C(8)	1.507(8)	1.473(9)
Fe(1)—C(15)	2.028(7)	2.034(7)	C(16)—C(17)	1.350(2)	1.390(1)	C(5)—C(6)	1.360(1)	1.419(9)
Fe(1)—C(16)	2.038(9)	2.027(8)	C(17)—C(18)	1.370(2)	1.380(1)	C(4)—C(5)	1.360(1)	1.390(1)
Fe(1)—C(17)	2.024(9)	2.038(7)	C(18)—C(19)	1.370(2)	1.390(1)	C(6)—C(1)	1.400(1)	1.360(1)
Fe(1)—C(18)	2.030(1)	2.046(8)	C(19)—C(20)	1.420(2)	1.430(2)	C(8)—C(21)	1.484(9)	1.480(1)
Fe(1)—C(19)	2.020(1)	2.029(8)	C(20)—C(16)	1.380(2)	1.380(1)	C(21)—C(22)	1.430(1)	1.430(1)
Fe(1)—C(20)	2.039(9)	2.045(8)	Fe(2)—C(21)	2.020(6)	2.029(8)	C(22)—C(23)	1.410(1)	1.440(2)
N(1)—N(2)	1.338(7)	1.320(8)	Fe(2)—C(22)	2.029(7)	2.050(1)	C(23)—C(24)	1.380(1)	1.320(3)
N(1)—C(1)	1.353(8)	1.384(8)	Fe(2)—C(23)	2.048(8)	2.020(1)	C(24)—C(25)	1.420(1)	1.400(2)
N(1)—C(7)	1.495(9)	1.474(8)	Fe(2)—C(24)	2.043(8)	1.980(2)	C(25)—C(21)	1.410(1)	1.420(1)
C(1)—C(2)	1.404(9)	1.390(1)	Fe(2)—C(25)	2.045(7)	2.040(1)	C(26)—C(27)	1.370(1)	1.350(2)
C(2)—C(3)	1.340(1)	1.370(1)	Fe(2)—C(26)	2.051(8)	2.015(9)	C(27)—C(28)	1.400(1)	1.390(2)
C(3)—C(4)	1.440(1)	1.370(1)	Fe(2)—C(27)	2.030(9)	2.010(1)	C(28)—C(29)	1.420(1)	1.360(2)
C(7)—C(11)	1.490(1)	1.503(9)	Fe(2)—C(28)	2.035(9)	2.020(1)	C(29)—C(30)	1.380(1)	1.410(2)
C(11)—C(12)	1.410(1)	1.410(1)	Fe(2)—C(29)	2.050(7)	2.036(9)	C(30)—C(26)	1.430(1)	1.350(2)

soluble in polar organic solvents and insoluble in water and in diethyl ether; when heated above 100 °C they decompose. The structures and compositions of these compounds were confirmed by elemental analysis and IR (Table 1), ^{1}H NMR (Table 2), and mass spectra.

The mass spectra exhibit molecular ions of the cationic parts of salts **1—8** and fragmentation products characteristic of ferrocene derivatives and nitrogen-containing components.

The IR spectra of the salts synthesized contain, along with the absorption bands typical of the ferrocene ring and other fragments (benzotriazolyl, azaferrocenyl, *etc.*), broad intense absorption bands in the BF_4^- stretching region (1110—1015 cm^{-1}).

^{1}H NMR spectra of salts **1—8** exhibit signals of the protons of unsubstituted (singlet) and substituted (multiplet) cyclopentadienyl rings and the signals corresponding to benzene rings and methyl, methylene, and methyne groups are the characteristic multiplets. The signals of the protons of salts **1—5** display the typical downfield shift with respect to the similar signals of neutral ferrocenylalkyl-substituted benzotriazoles.[11] The signals of the four protons of the benzotriazole moiety in the ^{1}H NMR spectrum of salt **1** form two symmetrical

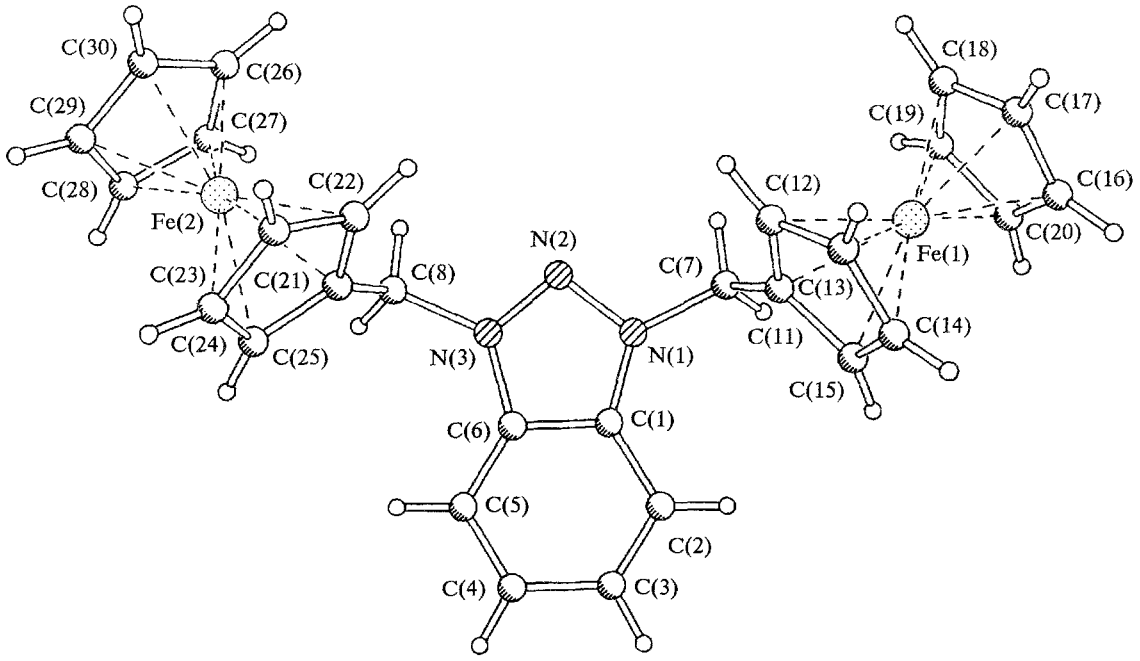


Fig. 1. The structure of the 1,3-bis(ferrocenylmethyl)benzotriazolium cation (**A**) in the crystal of **1** · 0.25 Me_2CO.

Table 4. The atomic coordinates ($\times 10^4$) in the structure of **1** · 0.25 Me_2CO

Atom	*x*	*y*	*z*	*x*	*y*	*z*
		Cation **A**			Cation **B**	
Fe(1)	4760(1)	7540(1)	5812(1)	242(1)	2723(1)	1334(1)
Fe(2)	−977(1)	8095(1)	2113(1)	5877(1)	848(1)	−1957(1)
N(1)	1750(4)	6400(4)	4876(3)	3205(4)	3588(4)	134(3)
N(2)	1476(5)	6832(4)	4109(3)	3598(5)	3230(4)	−532(3)
N(3)	429(5)	6809(4)	4107(3)	4640(5)	3167(4)	−526(3)
C(1)	887(5)	6279(5)	5355(4)	4171(5)	3758(5)	591(4)
C(2)	765(5)	5882(5)	6176(4)	4262(6)	4133(5)	1323(4)
C(3)	−242(6)	5753(6)	6435(4)	5289(6)	4229(6)	1570(4)
C(4)	−1155(6)	5971(6)	5911(5)	6171(6)	3957(6)	1146(5)
C(5)	−1027(6)	6344(5)	5117(4)	6106(5)	3566(6)	422(4)
C(6)	−5(5)	6483(5)	4847(4)	5038(5)	3477(5)	167(4)
C(7)	2918(5)	6420(5)	5076(4)	2146(5)	3745(5)	305(4)
C(8)	−125(6)	7125(5)	3307(4)	5214(6)	2803(6)	−1208(4)
C(11)	3232(5)	7262(5)	5526(4)	1774(5)	2946(5)	977(4)
C(12)	3486(6)	8273(6)	5176(4)	1486(5)	1935(5)	897(4)
C(13)	3765(7)	8813(6)	5819(6)	1191(6)	1419(5)	1663(5)
C(14)	3688(7)	8152(7)	6539(5)	1315(6)	2122(6)	2227(4)
C(15)	3349(6)	7199(6)	6375(5)	1663(5)	3055(6)	1802(4)
C(16)	6185(7)	7288(10)	6408(6)	−1162(6)	3067(8)	1865(5)
C(17)	6293(7)	7987(8)	5739(8)	−1313(5)	2310(6)	1382(5)
C(18)	6052(8)	7551(11)	5071(6)	−1057(6)	2714(6)	598(6)
C(19)	5777(7)	6555(11)	5335(9)	−723(6)	3718(7)	587(6)
C(20)	5858(7)	6375(8)	6189(8)	−811(6)	3947(7)	1393(7)
C(21)	−582(6)	8200(5)	3207(4)	5451(6)	1674(7)	−1064(4)
C(22)	9(6)	9120(6)	3048(4)	6481(8)	1182(10)	−896(5)
C(23)	−735(7)	9970(5)	2937(4)	6314(17)	93(14)	−858(7)
C(24)	−1750(7)	9599(6)	3025(4)	5293(16)	−36(10)	−1005(10)
C(25)	−1676(6)	8504(5)	3203(4)	4700(8)	906(7)	−1113(6)
C(26)	−44(7)	8800(7)	1130(4)	5834(12)	1844(8)	−3000(6)
C(27)	−701(9)	7987(7)	1317(5)	5145(9)	1087(12)	−3039(6)
C(28)	−1774(8)	8337(6)	1278(5)	5737(10)	156(8)	−2946(6)
C(29)	−1780(6)	9425(6)	1043(4)	6783(8)	348(8)	−2847(5)
C(30)	−727(7)	9710(6)	953(4)	6839(8)	1427(9)	−2884(5)
		Anion **A**			Anion **B**	
B	3242(10)	4073(8)	6977(7)	−1851(8)	3959(8)	−1787(6)
F(1)	4208(6)	4432(5)	6766(5)	−1821(5)	2945(4)	−1873(4)
F(2)	2799(6)	4727(6)	7434(4)	−2368(6)	4564(5)	−2411(3)
F(3)	3411(5)	3097(4)	7344(4)	−836(4)	4262(4)	−1725(4)
F(4)	2630(5)	4074(4)	6303(3)	−2401(4)	4087(4)	−1100(3)
		Acetone				
O	431(27)	8831(19)	5194(16)			
C(O-1)	69(39)	9534(20)	5117(17)			
C(O-2)	962(16)	10297(20)	4786(12)			

quadruplets, which suggests 1,3-substitution in this heterocycle.

To determine unambiguously the structures of the benzotriazolium salts **1—5** obtained, we carried out an X-ray structural study of compound **1**, which crystallizes from an acetone—heptane mixture as greenish-yellow lamellar crystals having the composition **1** · 0.25 Me_2CO. The independent part of a unit cell contains two 1,3-bis(ferrocenylmethyl)benzotriazolium cations and two BF_4^- anions (**A** and **B**) separated by normal van der Waals distances, and a disordered molecule of acetone of crystallization with a population of 50 %. This molecule is located near the inversion center in such a way that its methyl carbon atoms are connected by this center, and the C=O group is disordered at two positions that are also connected by the same inversion center. Both cations have similar conformations with a cisoid arrangement of the ferrocenyl groups with respect to the plane of the benzotriazole unit (Fig. 1). The C(1)N(1)C(7)C(11) torsion angles in cations **A** and **B** are −73.0 and −72.8°, and the C(6)N(3)C(8)C(21) angles are 80.3 and 87.7°, respectively. The angles of the inclination of the Cp rings with respect to the plane of the benzotriazole fragment are also similar to one another (70 and 67° in **A**, 72 and 64° in **B** for rings **D** and **E**, respectively). Thus, the intrinsic symmetry of each of the cations is approximately *m*.

The distance of the iron atom to the plane of the substituted Cp ring is somewhat greater than that to the plane of the unsubstituted Cp ring (the average values for molecules **A** and **B** are 1.654 and 1.643 Å), but the relative shortening of the C—C bonds in the latter is illusory and is caused by the intense heat motion. The bond lengths in both cations (Table 3) are close within the experimental error and are normal for ferrocene and benzotriazolium derivatives.

Experimental

IR spectra were recorded on a UR-20 spectrometer (Karl Zeiss). ^{1}H NMR spectra were obtained on Bruker WP-200 SY and Bruker WM-250 spectrometers. Mass spectra were obtained on Varian CH-8 and Kratos MS-890 mass spectrometers. The starting *N*-ferrocenylalkyl-substituted benzotriazole derivatives were prepared by the known procedure.[11] Azaferrocene was kindly provided by N. I. Pyshnograeva.

Preparation of 1,3-bis(ferrocenylalkyl)benzotriazolium tetrafluoroborates (1—5) was carried out according to a general procedure. A 48 % aqueous solution of HBF_4 (0.18 mL) was added to an intensely stirred mixture of an α-hydroxyferrocenyl derivative (1 mmol) and the corresponding *N*-ferrocenylalkyl-substituted benzotriazole (1 mmol) in 1 mL of CH_2Cl_2. The stirring was continued for 3—5 min, and 5—10 mL of diethyl ether was added. The resulting precipitate of a salt **1—5** was filtered off, washed with water and hexane, and dried over $CaCl_2$ *in vacuo*. The results of elemental analysis, yields, and IR spectra are presented in Table 1.

1,1′-bis[α-(3-Ferrocenylmethylbenzotriazolio-1)ethyl]-ferrocene bis-tetrafluoroborate (6). A 48 % aqueous solution of HBF_4 (0.36 mL) was added to a vigorously stirred solution containing 1,1′-bis(α-hydroxyethyl)ferrocene (1 mmol) and 1-(ferrocenylmethyl)benzotriazole (2 mmol) in 1.5 mL of CH_2Cl_2. After 5 min, the precipitate of salt **6** was filtered off, washed with water and hexane, and dried over $CaCl_2$ *in vacuo* (see Table 1).

1,1′-bis[α-(*N*-Hexamethylenetetramino)ethyl]ferrocene bis-tetrafluoroborate (7). A 48 % aqueous solution of HBF_4 (0.18 mL) was added to a vigorously stirred mixture containing 1,1′-di(α-hydroxyethyl)ferrocene (0.05 mmol) and 1-hexamethylenetetramine (urotropin) (1 mmol) in 2 mL of CH_2Cl_2. After 4 min, the precipitate of salt **7** was filtered off, washed with cold water and pentane, and dried over $CaCl_2$ *in vacuo* (see Table 1).

***N*-(α-Ferrocenylethyl)azoniaferrocene tetrafluoroborate (8)**. A 48 % aqueous solution of HBF_4 (0.18 mL) was added to a vigorously stirred solution containing azaferrocene (1 mmol) and α-hydroxyethylferrocene (1 mmol) in 1.5 mL of CH_2Cl_2. After 5 min, 10 mL of diethyl ether and 10 mL of water were successively added to the reaction mixture. After cooling to 0 °C, the precipitate was filtered off, washed with water and ether, and dried over $CaCl_2$ *in vacuo* (see Table 1).

The X-ray structural study of 1 · 0.25 Me_2CO. The unit cell parameters and the intensities of reflections were measured on a Siemens P3/PC four-circle diffractometer (293 K, λMo-*K*α = 0.71069 Å, graphite monochromator).

The crystals are triclinic, a = 12.498(2), b = 13.097(3), c = 16.743(4) Å, α = 81.34(2), β = 89.62(2), γ = 87.62(2)°, V = 2707(2) Å^3, space group $P\bar{1}$, Z = 4 $C_{28}H_{26}N_3Fe_2BF_4 \cdot 0.25\ C_3H_6O$, μ = 11.2 cm^{-1}, d_{calc} = 1.52 g·cm^3. The intensities of 5112 independent reflections with $I > 2\sigma(I)$ and $2\theta \leq 55°$ were measured by θ/2θ-scanning. The structure was solved by the direct method and refined by the full-matrix least-squares methods using the SHELXTL PLUS program package (the PC version).[15] All of the nonhydrogen atoms were refined in the anisotropic approximation (taking into account the contributions of H atoms fixed at the calculated positions) to R = 0.060 and R_w = 0.051. The weighing scheme $w = [\sigma^2(F)+0.0001F^2]^{-1}$ was used; the quality factor S = 1.76. The residual peaks of the electron density in the final differential synthesis did not exceed 0.30 e/ Å^3. The coordinates of the atoms are listed in Table 4.

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