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Synthesis, crystal and molecular structure of $[\{C_5Me_5FeC_5Me_4CH_2\}^+B\{C_6H_3(CF_3)_2\}_4^-]$, the first example of a structurally characterized primary ferrocenylcarbocation

Arkadii Z. Kreindlin *, Fedor M. Dolgushin, Aleksander I. Yanovsky, Zoya A. Kerzina, Pavel V. Petrovskii, Margarita I. Rybinskaya

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov St., Moscow 117813, Russia

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Abstract

The synthesis and the first X-ray structural study of a salt of the primary ferrocenylcarbocation $[\{C_5Me_5MC_5Me_4CH_2\}^+ B\{C_6H_3(CF_3)_2\}_4^-]$ (M = Fe, **1a**) are reported. The C_{Cp}–C_α bond shows considerable inclination relative to the plane of the cyclopentadienyl ring so that the C_α atom becomes closer to the metal centre, the inclination angle α being equal to 23.6°. The Fe–C_α distance (2.567(12) Å) is still significantly longer than the covalent Fe–C σ-bond, which may be considered as an indication that the donor–acceptor interaction of the carbocationic centre with the metal electron pair is substantially weaker than in the earlier studied Ru- and Os-analogues (**1b**, **1c**) wherein the positive charge was mostly localized on the metal centre (metallonium cations). Thus, complex **1a** obviously preserves much more of the carbocationic state than its heavier analogues.

Keywords: Carbocations; Metallonium cations; Iron; Crystal struture; NMR spectra; X-ray study

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1. Introduction

Earlier we reported the synthesis [1,2] and X-ray structural studies of the salts of permethylated primary cations $[(C_5Me_5MC_5Me_4CH_2)^+ BPh_4^-]$ (**1b**, M = Ru [3]; **1c**, M = Os [2]). Structural results showed that Ru- and Os-containing cations have a rather unusual geometry with the CH_2-group significantly displaced from the Cp-ring plane towards the metal atom. The C_{Cp}–C_α bond is inclined to the Cp-ring plane by 40.3 and 41.8° in the Ru- and Os-complexes respectively, and the M–C_α distances are equal to 2.270 (Ru) and 2.224 Å (Os) which are indeed quite close to the lengths of the corresponding M–C σ-bonds [4,5]. These results indicated effective interaction between the carbocationic centre and the lone electron pair (LEP) of the metal atom, which leads to the formation of a donor–acceptor bond and, ultimately, to the complete charge transfer from the carbon atom to the metal centre. This was also confirmed by the MO calculation carried out by the extended Hückel method [6]. It is noteworthy that this charge transfer process does not imply oxidation of the metal, but rather results in the increase of its coordination number; the $C_5Me_4CH_2$-ligand coordination may be described as either η^6 or σ,η^5. Thus, those cations should in fact be regarded not as carbocations but as true onium compounds, which we named metallonium cations by analogy with corresponding onium organic derivatives [7].

The structure of the Fe-containing cation **1a** (M = Fe) remained unknown for a long time because of the difficulties associated with the preparation of X-ray quality single crystals of its salts. It should be emphasized that the structure of permethylated Fe-containing primary carbocation is of substantial interest as a basis for theoretical treatment of the nature of chemical bonding in these ions. All available structural data were limited to systems with the substitution at the carbocationic centre, e.g. $C_5H_5FeC_5H_4CPh_2^+BF_4^-$ [8], $(C_5H_5FeC_5H_4)_2CH^+BF_4^-$ [9], and $(C_5H_5FeC_5H_4)C_3Ph_2^+BF_4^-$ [10]. The substituents inevitably cause notable

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* Corresponding author. Tel.: + 95-135-9308; fax: + 95-135-5085.
E-mail address: krekis@ineos.ac.ru (A.Z. Kreindlin).

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distortions of the geometry of the cation (vide infra) which made it so important to obtain the data for the primary carbocation. The difficulties with the preparation of the crystals of the salts of the **1a** cation were due primarily to the peculiar chemical behaviour of ferrocenylmethyl cations [11], i.e. their involvement in the redox tautomerism [12–14] of the monomer and subsequent dimerization both in solution and in the solid state:

$$C_5Me_5Fe{:}C_5Me_4CH_2^+An^- \ (\mathbf{1a}) \Leftrightarrow$$
$$C_5Me_5Fe^+{\cdot}C_5Me_4C{\cdot}H_2An^- \ (\mathbf{1a'})$$
$$\rightarrow \tfrac{1}{2}(C_5Me_5Fe^+{\cdot}C_5Me_4CH_2)_2An_2^- \ (\mathbf{2})$$

In the kinetic studies of the two-stage dimerization process we have shown that (a) the rate of the tautomerism and dimerization depends on the nature of the anion and decreases with the increasing bulk of the anion in the $BF_4^- > PF_6^- > AlBr_4^-$ series, and (b) the limiting stage of the process is the migration of the anion accompanied by the rearrangement of the crystal lattice [14]. The nature of the anion was found to play a significant role in the determination of the dimerization rate even in the solution. These data suggested that the stability of the salts **1a** increases in going to the bulkier anions characterized by lower migration rates.

2. Results and discussion

In contrast to tetraphenylborate (BPh_4), the tetrakis(3,5-bis(trifluromethyl)phenyl)borate anion which has eight trifluoromethyl substitutents ($[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]$), has only recently become an anion of choice for the preparation of a wide range of cationic complexes [15–19]. Its salts normally show better solubility in common organic solvents and higher stability even in strong acidic solutions than their tetraphenylborate analogues [15–19]. In the present work we prepared the salts of **1a** with both anions from $C_5Me_5FeC_5Me_4CH_2OH$ (**3**) according to the following reaction scheme:

$$C_5Me_5FeC_5Me_4CH_2OH \ (\mathbf{3}) + CF_3CO_2H \rightarrow$$
$$[(C_5Me_5FeC_5Me_4CH_2^+)CO_2CF_3^-]$$
$$[(C_5Me_5FeC_5Me_4CH_2^+)CO_2CF_3^-] + NaAn \rightarrow$$
$$[(C_5Me_5FeC_5Me_4CH_2) + An^-]$$
$$An = BPh_4, \ B\{C_6H_3(CF_3)_2\text{-}3,5\}_4$$

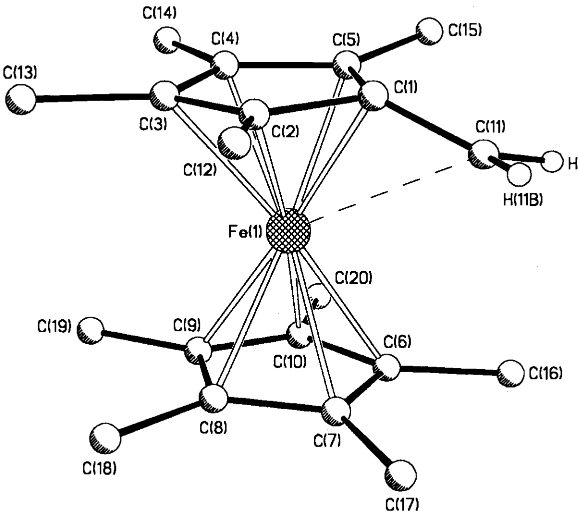

Fig. 1. Molecular structure of cation $[C_5Me_5FeC_5Me_4CH_2]^+$ (**1a**). Methyl H atoms are omitted for clarity.

The BPh_4 salt was obtained by the treatment of the alcohol **3** with the acetic acid doped by less than 5% of CF_3COOH and subsequent addition of the $NaBPh_4$ solution in AcOH. The $B\{C_6H_3(CF_3)_2\text{-}3,5\}_4$ salt was synthesized by protonation of **3** with CF_3COOH in CH_2Cl_2 and subsequent treatment by the solution of $NaB\{C_6H_3(CF_3)_2\text{-}3,5\}_4$ in CH_2Cl_2. The structure and composition of the **1a**·BPh_4 salt were confirmed by elemental analysis and the ^{1}H-NMR spectra (see Section 4). It was impossible to grow single crystals of this salt because of the dimerization process, even though this process is indeed much slower than in case of the salts with smaller anions like BF_4, PF_6, and $AlBr_4$. At the same time, we succeeded in growing the crystals of **1a**·$B\{C_6H_3(CF_3)_2\text{-}3,5\}_4$ suitable for the X-ray experiment. The orange crystals were obtained from the CH_3NO_2–Et_2O mixture at − 12° (in the freezer). It is important to mention that upon prolonged storage (more than 3 weeks at − 12°) the dimerization process does occur even in case of the **1a**·$B\{C_6H_3(CF_3)_2\text{-}3,5\}_4$ salt. This process causes both the crystals and the mother liquor to change colour from orange to green, which gives a clear indication of the above mentioned redox process and eventual formation of dimerization product **2**. The structure of **2** was assigned unambiguously on the basis of ^{1}H, ^{13}C, ^{11}B and ^{19}F-NMR spectra (see Section 4). It is also noteworthy that even at − 12° after 6 days (the time and conditions of the X-ray diffraction experiment) the crystals show definite signs of formation of **2**. It may be this dynamic process which accounts for the limited accuracy of the final X-ray structural results. The structure of cation **1a** in the crystals of its $B\{C_6H_3(CF_3)_2\text{-}3,5\}_4$ salt is shown in Fig. 1, bond lengths and main bond angles are listed in Table 1.

Earlier, in [7] we predicted the approximate Fe–C_α distance and the C_{Cp}–C_α-bond/Cp-plane inclination angle in the primary ferrocenylcarbocation and came up with the values of 2.5 Å and 25–30° respectively. The X-ray structural study gave the results of 2.567(12) Å for the Fe–C(11) distance and 23.6° for the inclination angle which thus shows a fairly good agreement with

Table 1
Bond lengths (Å) and selected bond angles (°) in **1a**

Fe(1)–C(1)	1.97(1)	C(3)–C(4)	1.46(1)
Fe(1)–C(2)	2.05(1)	C(3)–C(13)	1.53(1)
Fe(1)–C(3)	2.12(1)	C(4)–C(5)	1.42(1)
Fe(1)–C(4)	2.14(1)	C(4)–C(14)	1.47(1)
Fe(1)–C(5)	2.05(1)	C(5)–C(15)	1.51(1)
Fe(1)–C(6)	2.09(1)	C(6)–C(7)	1.43(1)
Fe(1)–C(7)	2.10(1)	C(6)–C(10)	1.43(2)
Fe(1)–C(8)	2.06(1)	C(6)–C(16)	1.51(1)
Fe(1)–C(9)	2.01(2)	C(7)–C(8)	1.37(2)
Fe(1)–C(10)	2.12(1)	C(7)–C(17)	1.51(2)
Fe(1)–C(11)	2.57(1)	C(8)–C(9)	1.40(2)
C(1)–C(2)	1.45(1)	C(8)–C(18)	1.54(2)
C(1)–C(5)	1.42(1)	C(9)–C(10)	1.41(2)
C(1)–C(11)	1.37(2)	C(9)–C(19)	1.49(2)
C(2)–C(3)	1.38(1)	C(10)–C(20)	1.47(2)
C(2)–C(12)	1.51(1)		
C(11)–C(1)–C(5)	122.3(10)	C(10)–C(6)–C(16)	125.4(10)
C(11)–C(1)–C(2)	122.6(11)	C(7)–C(6)–C(16)	124.8(10)
C(5)–C(1)–C(2)	108.9(9)	C(16)–C(6)–Fe(1)	130.7(8)
C(11)–C(1)–Fe(1)	98.9(11)	C(8)–C(7)–C(6)	108.2(10)
C(3)–C(2)–C(1)	107.1(9)	C(8)–C(7)–C(17)	122.8(12)
C(3)–C(2)–C(12)	127.9(10)	C(6)–C(7)–C(17)	129.0(12)
C(1)–C(2)–C(12)	124.9(10)	C(17)–C(7)–Fe(1)	129.1(9)
C(12)–C(2)–Fe(1)	128.7(8)	C(7)–C(8)–C(9)	107.1(10)
C(2)–C(3)–C(4)	109.4(9)	C(7)–C(8)–C(18)	127.3(14)
C(2)–C(3)–C(13)	126.3(9)	C(9)–C(8)–C(18)	125.5(14)
C(4)–C(3)–C(13)	124.1(10)	C(18)–C(8)–Fe(1)	125.9(10)
C(13)–C(3)–Fe(1)	130.8(8)	C(8)–C(9)–C(10)	112.2(11)
C(5)–C(4)–C(3)	106.9(9)	C(8)–C(9)–C(19)	126.9(13)
C(5)–C(4)–C(14)	127.9(10)	C(10)–C(9)–C(19)	120.6(13)
C(3)–C(4)–C(14)	125.2(10)	C(19)–C(9)–Fe(1)	126.1(11)
C(14)–C(4)–Fe(1)	129.9(9)	C(9)–C(10)–C(6)	103.1(10)
C(4)–C(5)–C(1)	107.6(9)	C(9)–C(10)–C(20)	131.7(12)
C(4)–C(5)–C(15)	125.2(10)	C(6)–C(10)–C(20)	125.1(11)
C(1)–C(5)–C(15)	127.0(10)	C(20)–C(10)–Fe(1)	127.3(9)
C(15)–C(5)–Fe(1)	129.7(8)	C(1)–C(11)–Fe(1)	49.2(10)
C(10)–C(6)–C(7)	109.3(10)		

the values predicted in [7]. It turns out that the M–C_α distance in the Fe-containing cation **1a** is considerably longer and the inclination angle α substantially smaller than in its Ru- (**1b**) and Os-analogues (**1c**). The Fe–C(11) distance in **1a** is also much longer than all other distances between the Fe atom and the carbon atoms of both Cp-rings (1.97(1)–2.14(1) Å), whereas the bond lengths M–C(11) in **1b** and **1c** are quite close to the range of distances found for M–C(*i*) (M = Ru, Os; *i* = 2–5). This leads to the conclusion that the M–C_α^+ interaction in **1a** is substantially weaker than that in its Ru- and Os-analogues (**1b**, **1c**). At the same time the donor–acceptor M–C_α^+ interaction in **1a** is undoubtedly stronger than in the tertiary cation salt $C_5H_5FeC_5H_4CPh_2^+BF_4^-$. The M–C(11) distance in the latter is equal to 2.715 Å [8]. Analogous relationships were also observed within the groups of Ru- and Os-containing compounds where the tertiary cation salts $C_5H_5MC_5H_4CPh_2^+PF_6^-$ (**4b**, **4c**) (**b** M = Ru, **c** M = Os) show longer M–C_α bonds and smaller inclination angles than corresponding salts of primary cations (2.482 and 2.387 Å, 34.0 and 38.4° for **4b** and **4c** respectively [20,21]). Geometrical parameters of cations **1a** and **4a** may be compared with those found in [22,23] for neutral chromium complexes $(CO)_3CrC_5H_4CH_2$ and $(CO)_3CrC_5H_4CPh_2$. The Cr–CH_2 and Cr–CPh_2 distances in these complexes are equal to 2.352 and 2.548 Å, the inclination angles α are equal to 35 and 31° respectively.

It seems worthwhile to consider also some other details of the structure and geometry of cation **1a** and its analogues **1b**, **1c**. In particular, the C(1)–C(11) bond length in **1a** is equal to 1.37(2) Å, whereas in **1b** [3] and **1c** [2] the corresponding bond length is equal to 1.401 and 1.426 Å, i.e. the certain lengthening of this bond accompanies the shortening of the M–C(11) distance in the Fe → Ru → Os series. This observation is in agreement with the calculated decrease in Mulliken bond orders for C(1)–C(11) bonds (1.14, 1.11 and 1.09) and the increase in bond orders for M–C(11) bonds (0.01, 0.16 and 0.22) from **1a** to **1b** and **1c** respectively (see [6]).

Complex **1a** is characterized by the small dihedral angle between the Cp-ring planes (4.7°); the corresponding dihedral angles in **1b** and **1c** are equal to 6.8 and 6.9° respectively. The C_5Me_4 moiety of the $C_5Me_4CH_2$ ligand is essentially planar, the displacement of the C(1) atom from the C(2)C(3)C(4)C(5) plane (0.02 Å) is within experimental error, the folding angle along the C(2)–C(5) line is equal to 1.4°.

A common structural feature for all cations **1a**–**1c** is a non-symmetrical position of the metal atom relative to the carbon atoms of the Cp-ring of the $C_5Me_4CH_2$ ligand. Thus, the Fe atom in **1a** is shifted from the centre of the Cp-ring of the C_5Me_4 ligand by 0.14 Å (this shift is measured as a distance between the projection of the metal atom onto the Cp-ring plane and the geometrical centre of the ring); the corresponding shifts for Ru (in **1b**) and Os (in **1c**) are equal to 0.20 Å. The shift of the Fe atom towards the C(1)–C(11) bond and the displacement of C(11) from the Cp-ring plane in the direction of the metal atom show correlation with the noticeable variations in the Fe–C_{Cp} distances. Thus, the Fe–C(1) distance (1.97(1) Å) is considerably shorter, the Fe–C(2) and Fe–C(5) distances (both 2.05(1) Å) are approximately equal, and the Fe–C(3) and Fe–C(4) bonds are longer than the average bond length for the Fe–C bonds involving the carbon atoms of the C_5Me_5 ligand.

The Cp-rings in cation **1a** are in the staggered conformation, the torsion angle C(1)X(1)X(2)C(9) (X(1) and X(2) refer to the centroids of the C(1)–C(5) and C(6)–C(10) rings respectively) is equal to 180°. Similar conformation was observed in **1b** and **1c** [2,3]. However, the tertiary cation $C_5H_5FeC_5H_4CPh_2^+$ (**4a**) with non-methylated Cp-rings has an almost eclipsed conformation (the corresponding torsion angle is equal to 153°).

The crystal structure of **1a**·B{$C_6H_3(CF_3)_2$-3,5}$_4$ is built of alternating cationic and anionic layers which are parallel to the crystalographic plane (010) (Fig. 2). All interionic distances in both layers correspond to the normal van der Waals contacts.

3. Conclusion

Summing up the obtained data one may conclude that the geometry of the Fe-containing cation differs considerably from the geometry of the Ru- and Os-analogues. In particular, in going from Ru and Os derivatives to the Fe complex the inclination angle of the C–CH_2 bond relative to the Cp-ring becomes smaller and the M–CH_2 bond becomes longer, so that the observed Fe–CH_2 distance in **1a** is almost 0.5 Å longer than the typical Fe–C σ-bond length (for example, 2.131 Å in Fe–CH_2R, where R = C_{sp2} [24]). This means that the Fe atom is involved in a relatively weak interaction with the carbocationic centre; according to the extended Huckel MO calculations the charge transfer from the carbocation to the metal centre does not exceed 10% [6]. Therefore, one may assume that this cation preserves its carbocationic nature to a far greater extent than its Ru and Os analogues. This is also confirmed in the chemical behaviour of the ferrocenylmethyl cation which, in contrast to the Ru- and Os-analogues, shows the ability for electron transfer from the metal atom to the carbocationic centre (redox process) with the formation of a cation-biradical species capable of dimerization (vide supra). Thus, results obtained show that the structure of primary Fe-containing cation may be interpreted in terms of the resonance hybrid **A** with greater contribution of carbocation form **A′**, than that of metallonium structure **A″**, which is caracteristic for Ru- and Os-containing cations:

$$\underset{\mathbf{A}}{C_5Me_5FeC_5Me_4C^+H_2\ (\mathbf{A'}) \leftrightarrow C_5Me_5Fe^+C_5Me_4CH_2\ (\mathbf{A''})}$$

4. Experimental

The ^1H, ^{13}C and ^{11}B-NMR spectra were recorded with the Bruker AMX-400 instrument at 400.13 MHz, with $BF_3 \cdot Et_2O$ as an external standard. The ^{19}F-NMR spectra were recorded using Bruker WP-200SY (188.31 MHz) with CF_3COOH as an external standard. The $NaB[C_6H_3(CF_3)_2]_4$ salt was obtained from the corresponding arylbromide according to [18]. The synthesis of **3** was reported earlier [14].

4.1. Salt *1a·B{$C_6H_3(CF_3)_2$-3,5}$_4$*

The solution of 266 mg (0.3 mmol) of NaB{$C_6H_3(CF_3)_2$-3,5}$_4$ in 30 ml of CH_2Cl_2 was added on stirring to the solution of 85 mg (0.25 mmol) of alcohol **3** in 30 ml of CH_2Cl_2 containing 0.3 ml of CF_3COOH. The mixture was stirred for 15 min and then evaporated to the minimum volume (approximately 5 ml). The addition of approximately 30 ml of pentane precipitated 230 mg (0.2 mmol) of the product (yield 86%). The orange–pink salt was dissolved in CH_3NO_2, treated with Et_2O and placed in the freezer. The crystals precipitated after about 24 h proved to be of sufficiently good quality for X-ray diffraction experiment. In about 3 weeks the crystals stored at − 12° turned green which indicated the formation of dimer **2**. The dimer was characterized by ^1H, ^{13}C, ^{11}B and ^{19}F-NMR spectra (vide supra) and elemental analysis. Found: C 50.87; H, 3.54; F, 38.57. Calc. for $C_{104}H_{82}B_2F_{48}Fe_2(CF_3COOH)$: C, 51.11; H, 3.36; F, 38.86%. ^1H-NMR spectra of this paramagnetic species show both cation (− 39.05 ppm ($\Delta\nu_{1/2}$ = 32 Hz, C_5Me_5,

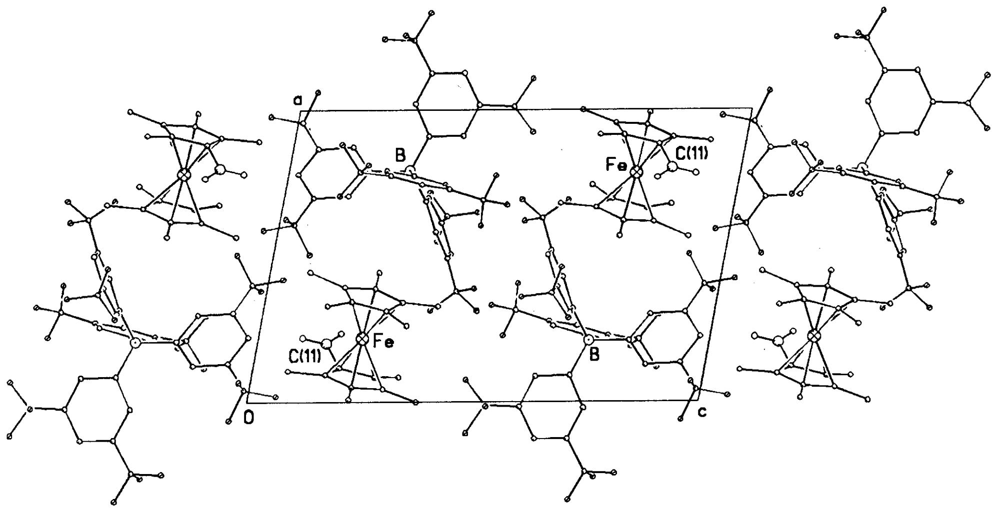

Fig. 2. Fragment of crystal packing of **1a**·B{$C_6H_3(CF_3)_2$-3,5}$_4$ projection onto the (010) crystallographic plane.

15H), -33.90 ppm ($\Delta\nu_{1/2} = 51$ Hz, C_5Me_4, 12H), -26.10 ppm ($\Delta\nu_{1/2} = 32$ Hz, CH_2CH_2, 1H), and -4.8 ppm ($\Delta\nu_{1/2} = 21$ Hz, CH_2CH_2, 1H)) and anion ($+7.62$ ppm ($\Delta\nu_{1/2} = 13$ Hz, *o*-H, 8H), $+7.67$ ppm ($\Delta\nu_{1/2} = 13$ Hz, *p*-H, 4H)) signals. The non-equivalence of diastereotopic protons of the CH_2CH_2 link is obviously due to the specific rotation of two $C_5Me_5FeC_5Me_4$-substituents about the $C_{CH2}{-}C_{CH2}$ bond. The ^{13}C-NMR spectra feature the cation (at -27.51 ppm ($\Delta\nu_{1/2} = 37$ Hz), -14.71 ppm ($\Delta\nu_{1/2} = 53$ Hz), $+29.25$ ppm ($\Delta\nu_{1/2} = 27$ Hz), $+161.32$ ppm ($\Delta\nu_{1/2} = 20$ Hz), $+252.19$ ppm ($\Delta\nu_{1/2} = 33$ Hz), $+277.08$ ppm ($\Delta\nu_{1/2} = 53$ Hz)) and anion (117.40 ppm (s, *p*-C), 124.42 ppm (q, CF_3, $J_{19F-13C}$ 271.8 Hz), 128.83 ppm (q, CCF_3, $J_{19F-13C}$ 30.5 Hz), 134.57 ppm (s, *o*-C), 161.51 ppm (q, CCF_3, $J_{11,10B-13C}$ 49.9 Hz)) signals. In the ^{11}B and ^{19}F-NMR spectra singlets at -6.727 ($\Delta\nu_{1/2} = 1.7$ Hz) and $+14.862$ ppm ($\Delta\nu_{1/2} = 22$ Hz) respectively are observed.

4.2. Salt **1a**·BPh_4

The solution of 0.206 g (0.6 mmol) of $NaBPh_4$ in 30 ml of AcOH was added on stirring to the solution of 0.17 g (0.5 mmol) of alcohol **3** in 30 ml of AcOH containing 0.5 ml of CF_3COOH. The precipitate was filtered, washed first with 5 ml of AcOH, and then three times with 10 ml of dry Et_2O and purified by precipitating with ether from CH_2Cl_2. 0.138 g (0.43 mmol) was obtained (yield 86%). Found: C, 81.39; H, 7.65. Calc. for $C_{44}H_{49}BFe$: C, 81.99; H, 7.66%. ^1H-NMR spectrum (δ): 1.28 (s, 6H, α-Me), 1.55 (s, 15H, Me), 1.92 (s, 6H, β-Me), 5.29 (s, 2H, CH_2^+), 7.2–7.5 (m, 20H, C_6H_5).

4.3. X-ray diffraction study

Crystals of **1a**·$B\{C_6H_3(CF_3)_2\text{-}3,5\}_4$ ($C_{20}H_{29}Fe(C_{32}H_{12}BF_{24})$) are triclinic, space group $P\bar{1}$, at 153 K. $a = 11.929(7)$, $b = 13.049(5)$, $c = 17.756(10)$ Å, $\alpha = 86.47(4)$, $\beta = 78.97(5)$, $\gamma = 80.08(4)°$, $V = 2671(3)$ Å^3, $Z = 2$, $D_{calc} = 1.522$ g cm^{-3}, $\mu = 4.04$ cm^{-1}. Intensities of 8427 independent reflections ($R_{int} = 0.042$) and cell parameters were measured at 153 K with a Siemens P3/PC diffractometer (graphite-monochromated Mo–K_α radiation, $\lambda = 0.71073$ Å, $\theta{-}2\theta$ scan technique, $\theta_{max} = 24°$). The structure was solved by direct method. With the exception of the carbon atoms in the anion, all non-hydrogen atoms were refined with anisotropic temperature factors. Two H atoms bonded to the C(11) atom were located in the difference Fourier synthesis and were included in the refinement with fixed positional and thermal parameters; all other H atoms were included in the least-squares refinement in the riding model approximation. Six peaks located in the difference Fourier synthesis most probably correspond to a disordered solvent molecule. We were not able to determine the exact formula of this solvent, however population of these positions with carbon atoms with s.o.f.s equal to 0.5 produced significant improvement both in the *R*-factor value and the overall accuracy of the structure. The final refinement of 568 parameters converged to $R_1 = 0.1132$ (on F for 3304 observed reflections with $I > 2\sigma(I)$) and $wR_2 = 0.3067$ (on F^2 for all independent reflections), the weight scheme used was $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + F_c^2)/3$, $a = 0.060$, $b = 5.000$. All calculations were performed on an IBM PC using the SHELXTL PLUS 5 program package [25].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 144753. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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