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Selective oxidants for organometallic compounds containing a stabilising anion of highly reactive cations: $(3,5(CF_3)_2C_6H_3)_4B^-)Cp_2Fe^+$ and $(3,5(CF_3)_2C_6H_3)_4B^-)Cp_2^*Fe^+$

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Abstract

A major interest in ferrocenium compounds arises from their usefulness as selective oxidants to prepare mixed-valence metallocenic stable compounds. In this paper, $Cp_2FeBAr'_4 = ((3,5(CF_3)_2C_6H_3)_4B^-)Cp_2Fe^+)$ (**a**), and $Cp_2^*FeBAr'_4 = ((3,5(CF_3)_2C_6H_3)_4B^-)\ Cp_2^*Fe^+)$ (**b**) are reported. These compounds have wide applications in the obtention of new organometallic salts with improved stability. The selective oxidation capacity of compounds **a** and **b** was investigated by the reaction of $[Cp^*Co^{II}(C_8H_6)Fe^{II}(C_8H_7)]$ with stoichiometric quantities of $Cp_2FeBAr'_4$ or $Cp_2^*FeBAr'_4$ where $[Cp^*Co^{III}(C_8H_6)Fe^{II}(C_8H_7)]BAr'_4$ was exclusively obtained. All salts that have BAr'^-_4 as counterion showed an enhanced solubility in low-polarity solvents, especially in diethyl ether. This fact allowed us to perform non-conventional measurements like cyclic voltammetry in diethyl ether as solvent with $NaBAr'_4$ as supporting electrolyte. Single-crystal structural determination of **a** and **b** was also achieved. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Oxidants; Ferrocenium; Inert anion

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1. Introduction

The ferrocenium ion $[Cp_2Fe]^+$ is a mild one-electron, outer-sphere oxidant, which has found widespread applications in stoichiometric and catalytic oxidation [1]. The ferrocenium ion is particularly useful where selective oxidation is required, for example, in the synthesis of mixed-valence complexes [2]. At the same time, is a useful building block in the synthesis of new magnetic materials [3] or in the preparation of mixed-valence compounds with expected conducting properties (new unidimensional materials) [4]. The cation almost invariably behaves as an innocent one-electron oxidant, an observation that was experimentally clarified in the comparative studies of the oxidative activation of C–H by $(CPH_3)^+$ and $(Cp_2Fe)^+$ [5]. Systematic variation of Cp-ring substituents enables the redox potential to be tailored to the particular need by providing a range of half-wave potentials (vs. calomel electrode) of -0.63 V for $[(C_5H_4NMe_2)_2Fe]$ and of 0.64 V for $[(C_5H_4CF_3)_2Fe]$ [6]. These substitutions also influence other physicochemical properties as evidenced by the bulky pentamethylcyclopentadienyl ligand (Cp*), which gives higher solubility and greater kinetic and thermodynamic stability on its oxidised iron complexes as compared with $[Cp_2Fe]$ [6,7].

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Ferrocenium salts incorporating a large variety of counterions, such as $(BF_4)^-$, $(PF_6)^-$, and $(BPh_4)^-$ or $(SbF_6)^-$, are well known [6,8–10]. Air stability, as well as solubility, greatly depends on the nature of the anion employed [6,11]. For example, $(Cp_2Fe)PF_6$ is barely soluble in coordinating solvents whereas the counterion BF_4^- improves the solubility markedly. The general low solubility of these ferrocenium salts in coordinating solvent requires oxidation to be performed under heterogeneous conditions. Beside, there is large evidence in the literature that in some complexes, where the designated counterions were expected to be inert, they react with the organometallic complexes [12–15].

Usually, in an organometallic redox reaction where the oxidant is ferrocenium, the products are ferrocene and an organometallic salt that contains the inert counterion (Reaction (1)):

$$Cp_2FeX + A \rightarrow AX + Cp_2Fe \qquad (1)$$

where X = inert counterion and A = organometallic compound.

In numerous cases the new salt AX presents poor solubility in common organic solvents, preventing a good characterisation of the saline derivative [16].

Our interest in ferrocenium compounds arises from their usefulness as selective oxidants to prepare mixed-valence metallocenic stable compounds (AX) [17], which are useful building blocks for the synthesis of novel materials with magnetic properties and in the construction of one-dimensional polymetallic conducting arrays [4]. Difficulties in the past to cleanly produce and to isolate some of these materials (attributed to the poor solubility properties either of the salt AX and/or kinetic instability) have stimulated our search for alternative reagents.

$(3,5(CF_3)_2C_6H_3)_4B^-$, an inert, non-coordinating anion, has found widespread use in the stabilisation of highly reactive cationic species [18–20]. Aside from improving chemical stability, salts containing this bulky anion show enhanced solubility in relatively non-polar solvents [21], prompting us to prepare ferrocenium derivatives incorporating this anion, and to investigate their synthetic usefulness.

2. Results and discussion

2.1. Synthesis of $[Cp_2FeBAr'_4]$ (**a**) and $[Cp^*_2FeBAr'_4]$ (**b**)

The ferrocenium salt can be prepared by two alternative methods:

1. by a metathesis reaction between ferrocenium tetrafluoroborate, Cp_2FeBF_4, and the $NaBAr'_4$ salt;
2. by one-electron oxidation of ferrocene with *p*-benzoquinone in the presence of the $HBAr'_4$ acid.

The decamethyl ferrocenium salt was prepared by method (2) as the corresponding tetrafluoroborate salt is not easily accessible.

The metathesis reaction in method (1) readily gives a high yield (> 90%) of the $[Cp_2Fe]^+[BAr'_4]^-$ salt. It involves the treatment under reflux of one equivalent of the sodium salt, $NaBAr'_4$, with one equivalent of the ferrocenium tetrafluoroborate in dichloromethane, removal of solvent in vacuum and extraction of the product with diethyl ether. Further filtration of the sodium tetrafluoroborate salt and precipitation of the corresponding ferrocenium with pentane renders the compound with high purity.

By method (2), both ferrocenium salts can be obtained in good yield (> 85%) by mixing 1 mol of a dichloromethane solution of the corresponding ferrocene with a dichloromethane solution that contains 1 mol of the acid, $HBAr'_4$, and 0.5 mol of *p*-benzoquinone. Addition of pentane to the resulting dark solution gives a precipitate of the ferrocenium salt.

We found that for the ferrocenium salts synthesis, the acid $HBAr'_4$, can be prepared either from the sodium salt and HCl gas as reported originally [21], or by using the stoichiometric amount of concentrated aqueous HCl.

The ferrocenium salts can be recrystallised by slow diffusion of pentane into a concentrated dichloromethane solution of **a** or **b**. The $[Cp_2FeBAr'_4]$ is obtained as blue crystals while $[Cp^*_2FeBAr'_4]$ as green crystals, and both are remarkably soluble in diethyl ether. The crystalline salts are thermally stable, remaining analytically pure (C and H analysis) when stored in air for at least one month.

The ferrocenium salt characterisation was accomplished by elemental analysis and by IR spectroscopy (KBr pellet). The IR spectra show the characteristic bands of the anion at 1355, 1277 and 1121 cm^{-1} for **a** and 1356, 1276 and a broad band 1161–1120 cm^{-1} for **b** (see Table 1 for crystal data and structure refinement of **a** and **b**).

The usefulness of both ferrocenium salts as selective oxidants was checked for the paramagnetic complex $[Cp^*Co(C_8H_6)Fe(C_8H_7)]$ [4]. The oxidation of 1 mol of $[Cp^*Co(C_8H_6)Fe(C_8H_7)]$ with 1 mol of $Cp_2FeBAr'_4$ or $Cp^*_2FeBAr'_4$ gave the diamagnetic-oxidised derivative $[Cp^*Co(C_8H_6)Fe(C_8H_7)]BAr'_4$ where only the cobalt was oxidised. It was characterised by ^1H- and ^{13}C-NMR spectroscopy (see Section 3).

The corresponding salt $[Cp^*Co(C_8H_6)Fe(C_8H_7)]BAr'_4$ showed more solubility and stability than the analogous $[Cp^*Co(C_8H_6)Fe(C_8H_7)]BF_4$ salt [4]. The enhanced solubility in different solvents is a general behaviour of AX compounds when $X = BAr'^-_4$ [18–20]. In particular, most of the salts of this anion show a high solubility in diethyl ether as shown in Table 2.

Table 1
Crystal data and structure refinement for $(3,5(CF_3)_2C_6H_3)_4B)Cp_2Fe$ and $(3,5(CF_3)_2C_6H_3)_4B)Cp_2^*Fe$

	$(3,5(CF_3)_2C_6H_3)_4$-B)Cp_2Fe (**a**)	$(3,5(CF_3)_2C_6H_3)_4$-B)Cp_2^*Fe (**b**)
Empirical formula	$C_{42}H_{22}BF_{24}Fe$	$C_{52}H_{42}BF_{24}Fe$
Formula weight	1049.26	1189.52
Temperature (K)	293(2)	294(2)
Wavelength (Å)	0.71069	0.71069
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions		
a (Å)	13.043(3)	13.119(4)
b (Å)	13.342(3)	35.254(6)
c (Å)	14.563(5)	11.784(3)
α (°)	93.07(2)	90
β (°)	90.19(2)	97.48(1)
γ (°)	118.68(2)	90
Volume (Å^3)	2218.9(10)	5404(2)
Z	2	4
D_{calc} (Mg m^{-3})	1.570	1.462
Absorption coefficient (mm^{-1})	0.471	0.397
$F(000)$	1042	2404
Crystal size (mm)	0.58 × 0.29 × 0.11	0.50 × 0.48 × 0.06
θ Range for data collection (°)	1.40–24.98	1.16–24.99
Index ranges	$-15\leq h\leq 15$, $-15\leq k\leq 15$, $0\leq l\leq 17$	$0\leq h\leq 15$, $0\leq k\leq 41$, $-14\leq l\leq 13$
Independent reflections	7786	9917
Absorption correction	Empirical	Emprical
Max and min transmission	0.999 and 0.923	0.999 and 0.936
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	7786/49/720	9324/55/772
Goodness-of-fit on F^2	0.932	1.029
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0748$, $wR_2 = 0.2084$	$R_1 = 0.0855$, $wR_2 = 0.2329$
R indices (all data)	$R_1 = 0.1407$, $wR_2 = 0.2237$	$R_1 = 0.2651$, $wR_2 = 0.5339$
Largest difference peak and hole (e Å^{-3})	0.520 and −0.378	0.436 and −0.317

2.2. Cyclic voltammetry (CV) analysis

In electrochemistry, the use of solvents with polarities less than those of CH_2Cl_2 and THF is quite difficult because the electrolyte salt must dissolve and appreciably dissociate in order to render the solution conducting. A potential benefit from the use of low-polarity solvents could be an increase in the chemical stability of the product, since displacement of ligands from the primary redox product should be less prone due to the lower coordinating properties of the solvent.

The enhanced solubility of the ferrocenium salts containing the anion $[BAr'_4]^-$ as counteranion, as well the high solubility of the sodium salt ($NaBAr'_4$) in diethyl ether, suggested the possibility of using this less polar medium to perform the cyclic voltammetry using the sodium salt as supporting electrolyte and as a counteranion to stabilise the oxidised species.

Prior to studying the electrochemical behaviour of the ferrocenium salts **a** and **b** in diethyl ether, a cyclic voltammogram of a 0.2 M solution of $NaBAr'_4$ in this medium was traced. This system provides an electrochemical window from 1.80 to −1.60 V vs. SCE, which is adequate for the study of these complexes. With the same electrolyte using dimethyl formamide as solvent, a window from 1.00 to −1.70 V vs. SCE is obtained.

Then the cyclic voltammograms of **a** and **b** in diethyl ether (0.2 M $NaBAr'_4$) (see Fig. 1(a and b)) and dichloromethane (0.2 M tetrabutylammonium tetrafluoroborate) were recorded. For both ferrocenium salts, one redox pair was observed corresponding to the oxidation (Fe^{2+}/Fe^{3+}) and its respective reduction. Complex **a** in diethyl ether has an $E_{1/2}$ value of 0.44 V ($v = 50$ mV s^{-1} vs. SCE), while complex **b** has an $E_{1/2}$ of −0.12 V ($v = 50$ mV s^{-1} vs. SCE). In dichloromethane (DCM), complex **a** has an $E_{1/2}$ value of 0.46 V ($v = 50$ mV s^{-1} vs. SCE), while complex **b** has an $E_{1/2}$ of −0.01 V ($v = 50$ mV s^{-1} vs. SCE).

In both solvents the ratio $i_{pc}/i_{pa} = 1$ was obtained, indicating that the oxidation products are chemically stable. With the purpose of corroborating the reversibility of the system, ferrocene was added to both solvents. The potential redox pair of ferrocene in diethyl ether is 0.49/0.38 vs. SCE ($E_{1/2} = 0.44$ V) and in DCM 0.52/0.40 vs. SCE ($E_{1/2} = 0.46$ V). A DE value of 100 mV for both systems, is slightly superior to the expected for a reversible process (60 mV) and it could be due either to the resistance of the reference electrode cell or to the limited conductivity of the solution.

The stability of these complexes in both solvents is very similar. However both compounds are more difficult to oxidise in DCM. $Cp_2FeBAr'_4$ is oxidised at a more positive potential in DCM than in diethyl ether ($\Delta E_{1/2} = 20$ mV). For $Cp_2^*FeBAr'_4$, $\Delta E_{1/2} = 110$ mV.

Table 2
Solubility in diethyl ether

Compound	Solubility at 0°C (g l^{-1})	Solubility at 0°C (M)	Solubility at 25°C (g l^{-1})	Solubility at 25°C (M)
$NaBAr'_4$	237.04	0.268	364.12	0.411
$Cp_2FeBAr'_4$	73.06	0.070	84.02	0.080
$Cp_2^*FeBAr'_4$	20.07	0.017	25.5	0.021

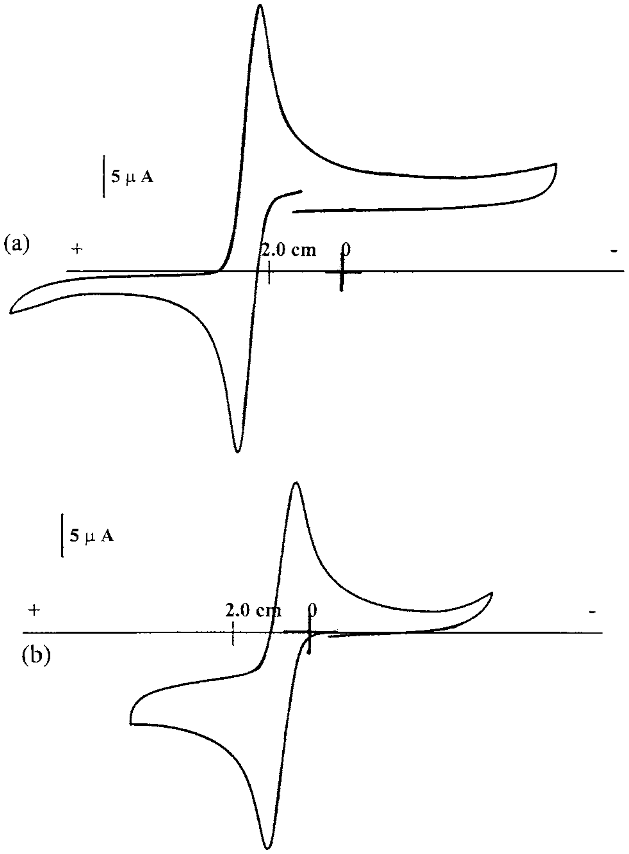

Fig. 1. Cyclic voltammetry of $Cp_2FeBAr'_4$ (a) and $Cp^*_2FeBAr'_4$ (b) in diethyl ether. Scan rate 0.2 V s^{-1}. Supporting electrolyte $NaBAr'_4$ 0.2 M. Working electrode platinum disc.

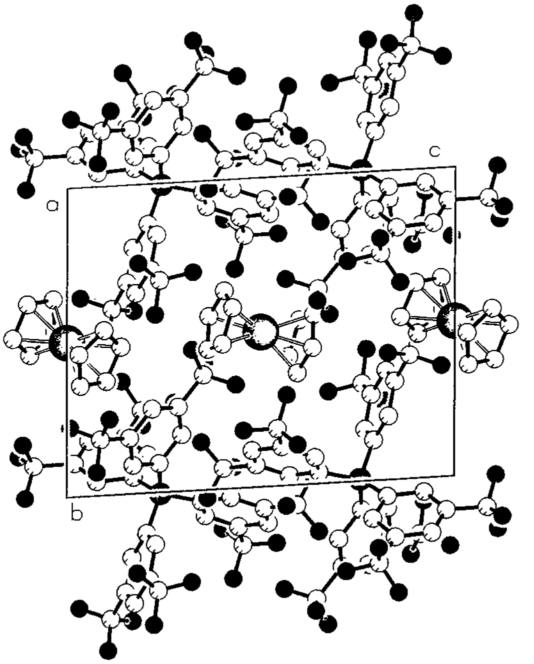

Fig. 2. Perspective view of the unit cell of $Cp_2FeBAr'_4$ along the x-axis.

2.3. X-ray structural characterisation

The crystal structures of the two complexes could be described as packing of alternated layers of cations and anions (see Figs. 2 and 3). The CF_3 groups of the anion present orientational disorder in both compounds as being usual in many structures containing this group. Concerning the cation, different conformations are present in each crystal structure.

In **a**, an average staggered conformation has been found, being the Fe atom on an inversion centre. The thermal ellipsoids are elongated with U_{33}/U_{11} ratios close to five. Two kinds of disorder can be considered according to U_{33} directions, a dynamic disorder involving a rotation or a libration of the rings about an axis perpendicular to the rings and containing the Fe atom, and a static disorder emerging of different sandwich conformations (see Fig. 4).

In **b**, one of the two rings of the cation is disordered. A model with two conformations with identical occupancy (SOF = 0.5) has been refined. One of them is staggered and the other is partly eclipsed (their relative orientation angles are 33.3 and 18.3°). Although more conformations exist there, only the mean is observed. This kind of disorder is frequent in other metallocenes [22–24].

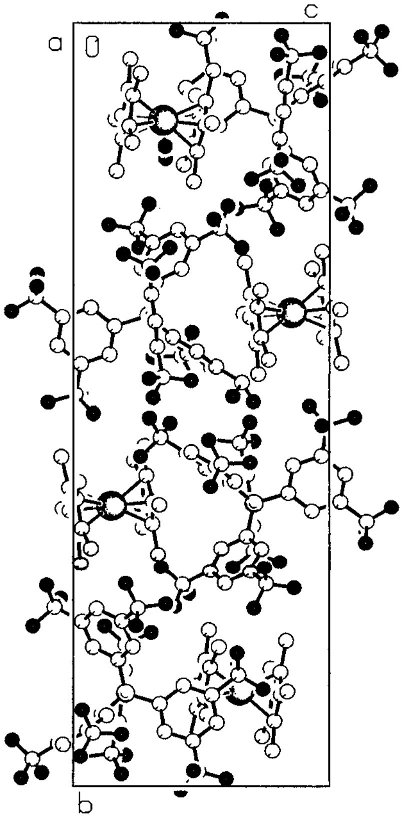

Fig. 3. Perspective view of the unit cell of $Cp^*_2FeBAr'_4$ along the x-axis.

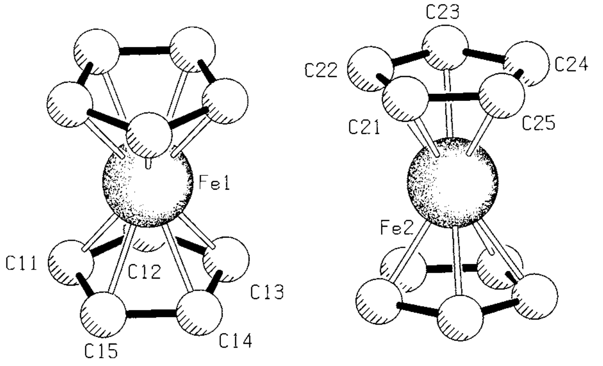

Fig. 4. Perspective view of two $Cp_2FeBAr'_4$ cations of the asymmetric unit.

All Fe–C distances are similar to those described in the literature [23]. The distances between the Fe atoms and the ring mean planes are 1.700 (**a**) and 1.609 Å (**b**) (see Fig. 5).

3. Experimental

3.1. General

All reactions were carried out using Schlenk techniques under a nitrogen atmosphere and the products were subsequently handled in a dry, oxygen-free glovebox. $NaBAr'_4$ and $HBAr'_4(Et_2O)_2$ were prepared following published procedures [21]. 3,5-bis(trifluoromethyl)-bromobenzene, $NaBF_4$, *p*-benzoquinone (used as sublimed), DCM, HCl (analysed) and pentane were from Merck. Diethyl ether was from Riedel of Häen. Cp_2FeBF_4 and Cp_2^*Fe were prepared in the laboratory. IR spectra were recorder on a Perkin–Elmer 1710 FT spectrophotometer using KBr pellets. Elemental analyses were obtained with a Fison 1108 microanalyser. ^{1}H-NMR spectra were determined using a Brucker ACT insstrument, 200 MHz.

Cyclic voltammetric (CV) measurements were carried out with a Potentiostat Bank (model Wenking ST-72) coupled to a Voltage Scan Generator (model USG-72) and a Graphtec Recorder (model WX-1100). The working electrode used in the CV was a platinum inlay electrode (Beckman). The auxiliary electrode was a platinum-coil electrode, which was isolated from the bulk solution by a glass tube with a porosity glass frit at the end; it contained a 0.2 M solution of supporting electrolyte. The reference was an Ag/AgCl (aqueous tetramethylammonium chloride) cracked glass bead electrode, which was adjusted to 0.00 versus the saturated calomel electrode (SCE). The reference electrode was located inside a Luggin capilar in the cell compartment. All the experiments were performed under an argon atmosphere, at room temperature (r.t., 20°C) in dichloromethane solution. Solutions were 3 mM in complex and 200 mM in tetraethylammonium tetrafluoroborate (TBA TFB) as the supporting electrolyte.

3.2. Preparation of $Cp_2FeBAr'_4$ (**1**) by metathesis

Cp_2FeBF_4 (0.520 g, 1.91 mmol) dissolved in CH_2Cl_2 (60 ml) was added to $NaBAr'_4$ (1.690 g, 1.91 mmol) and the mixture was heated under reflux for 30 min. The solvent was removed in vacuum and the product was extracted with diethyl ether. The diethyl ether was concentrated in vacuum to ca. 10 ml. Pentane (70 ml) was added and the blue precipitate which formed was filtered, washed with pentane and then dried in vacuum. The solid was recrystallised by slow diffusion of pentane into a concentrated dichloromethane solution. After 24 h the blue crystals (91%) were washed with pentane and dried in vacuum. IR (KBr pellet): 1355 (s), 1277 (s), 1121 (s, br) cm^{-1}. Anal. Calc. for $C_{42}H_{22}BF_{24}Fe$: C, 48; H, 2.09. Found: C, 47.7; H, 2.1%.

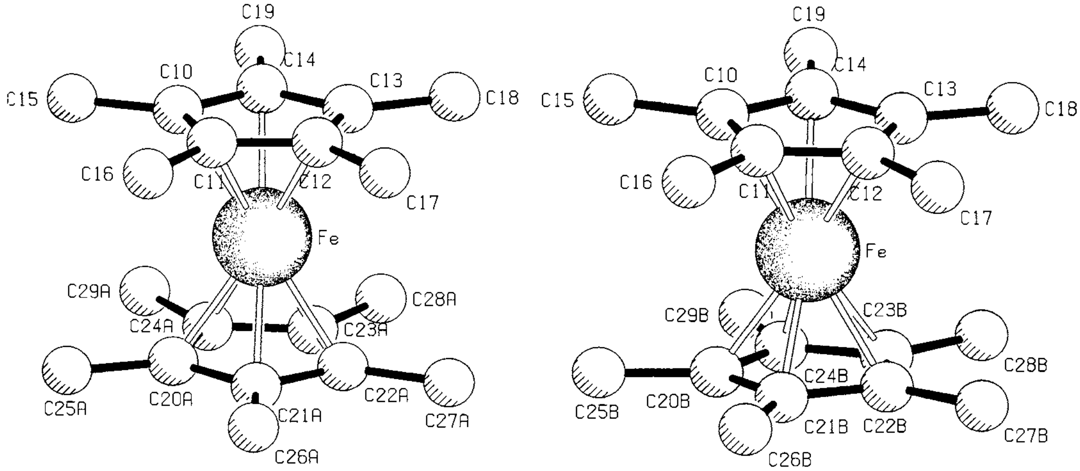

Fig. 5. Perspective view of the $Cp_2^*FeBAr'_4$ cation indicating the two orientations of the disordered Cp* ring.

3.3. Synthesis of $Cp^*_2FeBAr'_4$ (***b***) by oxidation of $[C_5(CH_3)_5]_2Fe$ with *p*-benzoquinone

$[C_5(CH_3)_5]_2Fe$ (0.368 g, 1.13 mmol) dissolved in CH_2Cl_2 (15 ml) was added slowly to CH_2Cl_2 (15 ml) containing 1,4 *p*-benzoquinone fresh sublimated (0.06 g, 0.57 mmol) and $HBAr_4(OEt_2)$ (1.146 g, 1.13 mmol). The mixture was stirred at room temperature (r.t.) for 1 h. The solvent was removed in vacuum and concentrated to ca. 10 ml. Pentane (40 ml) was added and the green precipitate that formed was filtered, washed with pentane and then dried in vacuum. The solid was recrystallised by slow diffusion of pentane into a concentrated dichloromethane solution. After 24 h the green crystal (86%) was filtered, washed with pentane and dried in vacuum. IR (KBr pellet) 1356 (s), 1276 (s), 1161–1120 (br) cm^{-1}. Anal. Calc. for $C_{52}H_{42}BF_{24}Fe$: C, 52.46; H, 3.53. Found: C, 52.42; H, 3.52%.

3.4. Synthesis of $Cp_2FeBAr'_4$ by oxidation of $[C_5(CH_3)_5]_2Fe$ with *p*-benzoquinone

This complex was prepared in 82% yield in a manner identical to that used for **b**.

3.5. Alternative synthesis of $HBAr'_4$

To a solution of $NaBAr'_4$ (3.37 g, 3.8 mmol) in diethyl ether (200 ml), cooled to −78°C, was added concentrated aqueous HCl (0.4 ml, 32%, 4 mmol) via syringe. The mixture was allowed to warm to 0°C and stirred for 30 min at this temperature. The formed NaCl was removed by filtration and the solution was allowed to stand for 12 h over 4 Å molecular sieves. The clear solution was then decanted via cannula to a separate flask and the solvent evaporated under reduced pressure to give $HBAr'_4\,(Et_2O)_2$ in 90% yield. The IR spectrum showed a trace of water, but this does not interfere with the ferrocenium synthesis.

3.6. Synthesis of $[Cp^*Co(C_8H_6)Fe(C_8H_7)]BAr'_4$

A solution of $[Cp^*Co(C_8H_6)Fe(C_8H_7)]$ (150 mg, 0.330 mmol) in diethyl ether (15 ml) was added to Cp_2FeBAr_4 (346 mg, 0.330 mmol) and the mixture was stirred at r.t. for 30 min resulting in the formation of a blue solution. Petroleum ether (45 ml) was added and the precipitate that formed was filtered, washed with petroleum ether, and then dried in vacuum. The solid was recrystallised by slow diffusion of petroleum ether into a concentrated diethyl ether solution of $[Cp^*Co(C_8H_6)Fe(C_8H_7)]BAr'_4$. Blue crystals (85%) were observed within 24 h. The crystals were filtered, washed with petroleum and dried in vacuum. Anal. Calc. for $C_{58}H_{36}BF_{24}FeCo$: C, 52.84; H, 3.06. Found: C, 52.65; H, 3.02%. ^{1}H-NMR (CD_2Cl_2) δ: 1.60 (s, 15H, Cp*), 2.67 (m, 2H), 3.8 (t, 1H), 4.2 (t, 1H), 4.3 (d, 1H), 4.5 (d, 1H), 4.6 (t, 1H), 5.0 (d, 1H), 5.1 (d, 1H), 5.2 (t, 2H), 6.17–6.30 (dd, 2H), 7.57 (s, 4H, BAr'_4) and 7.73 (s, 8H, BAr'_4).

IR (Nujol) cm^{-1}: 1612.3 (w), 1284.5 (s, BAr'_4), 1154–1133.9 (vs, BAr'_4), 887 (m), 839.1 (w), 807.8 (w), 725.4 (m), 714.4 (m), 682.1 (m), 669.2 (m).

3.7. Crystal structure determinations for $Cp_2FeBAr'_4$ (***a***) and $Cp^*_2FeBAr'_4$ (***b***)

Crystals of **a** and **b** suitable for single-crystal X-ray diffraction experiments were obtained by slow diffusion of pentane into a concentrated CH_2Cl_2 solution of the respective ferrocenium salt. Crystal data and details of the structure solutions are summarised in Table 1.

For both compounds data were collected at r.t. on an Enraf–Nonius CAD4 diffractometer. The following experimental set-up was used: graphite-monochromated Mo–K_α radiation, scan-mode $= \omega - 2\theta$, scan-width $= 0.80 + 0.35\,\mathrm{tg}\,\theta$ and scan-speed of 1.3–5.5° min^{-1}. Structures were solved by direct methods (SHELXS-86 program) [25] and full-matrix least-squares refinement on F^2 for all reflections (SHELXL-93 program) [26] was used.

Cyclopentadienyl, pentamethylcyclopentadienyl and phenyl groups were refined as rigid groups. The CF_3 groups were highly disordered. We modelled the disorder using some rigid groups (two or three) for each CF_3 and refining a torsion angle for every rigid group. The analysis of thermal parameters revealed structural disorder for pentamethylcyclopentadienyl and cyclopentadienyl groups. In this latter case, the disorder was not modelled, but in the case of **b** one pentamethylcyclopentadienyl group was split. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions with isotropic temperature factors fixed at 1.5 times (methyl hydrogens) or 1.2 times (the rest) U_{eq} of the corresponding carbon atoms. The weighting scheme $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

For **a**, $a = 0.1444$, $b = 0$. Final $R(F)$ and $R_w(F^2)$ values were 0.0748 and 0.2084 for reflections with $F_o^2 > 2\sigma(F_o^2)$.

For **b**, $a = 0.145$, $b = 11.6987$. Final $R(F)$ and $R_w(F^2)$ values were 0.0854 and 0.2336 for reflections with $F_o^2 > 2\sigma(F_o^2)$.

4. Conclusions

The well-known selective capacity of oxidation of ferrocenium, together with the stability given by the BAr'^- anion to the salts containing such anions, will enable a wide range of applications in organometallic synthesis. The more useful applications could be either in the preparation of oxidised compounds or in the preparation of mixed-valence complexes. These salts can be prepared by chemical methods using the oxidation with the ferrocenium or could be obtained 'in-situ' by electrochemical methods.

5. Supplementary material

Full details of the atomic parameters and bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 138350 and 138351 for $Cp_2FeBAr'_4$ and $Cp^*_2FeBAr'_4$, respectively). 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 www: http://www.ccdc.cam.ac.uk).

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