

# Difference in reactivity of triel halides $EX_3$ towards ferrocene

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## Abstract

A facile route to the  $Fe^{2+}$ -arene complex  $[(C_6H_6)FeCp][AlBr_4]$  is the reaction of ferrocene with  $AlBr_3$  in benzene. The structure of the  $Fe^{2+}$ -arene complex  $[(C_6H_6)FeCp][AlBr_4] \cdot C_6H_6$  was found to be isomorphous with those of  $[FeCp_2][ECl_4] \cdot C_6H_6$  ( $E = Al, Ga$ ). The crystal structures of the  $[FeCp_2][AlCl_4] \cdot C_6H_6$  ( $E = Al, Ga$ ) presented here show structural features which are different from those of solvent-free ferrocenium salts  $[FeCp_2][ECl_4]$  ( $E = Al, Ga, Fe$ ). However, the cell parameters of solvent-free ferrocenium tetrafluoroborate  $[FeCp_2][BF_4]$  are also quite different from those of solvent-free  $[FeCp_2][ECl_4]$  ( $E = Al, Ga, Fe$ ). In contrast to the eclipsed conformation in solvent-free  $[FeCp_2][ECl_4]$  ( $E = Al, Ga, Fe$ ) the cyclopentadiene rings in  $[FeCp_2][BF_4]$  and  $[FeCp_2][ECl_4] \cdot C_6H_6$  ( $E = Al, Ga$ ) are in a staggered conformation.

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**Keywords:** Ferrocene; Triel halides; Ferrocenium; Isomorphism

## 1. Introduction

A number of studies have shown that an electrophilic substitution of ferrocene takes place in the presence of  $BX_3$  ( $X = Cl, Br$ ) [1–3]. The mono and diborylated ferrocene (**1** and **2**), therefore, are accessible in high yield by treatment of ferrocene with 1 and 2 equiv. of  $BBr_3$ , respectively [2]. On the other hand, borylation with an excess of  $BBr_3$  results in the formation of tetraborylated ferrocene **3** [3]. However, our efforts to synthesize the related ferrocene derivatives with  $GaCl_2$  substituents on the Cp ring failed [4]. When an equimolar mixture of ferrocene and  $GaCl_3$  is treated with benzene, blue green crystals of  $[FeCp_2][GaCl_4]$  and red platelets of the multidecker sandwich complex **4** were obtained, as depicted in Scheme 1 [4]. This leads to the conclusion that a redox reaction, by which ferrocene is oxidized to ferrocenium cation and  $Ga(III)$  is reduced to  $Ga(I)$ , takes place.

Up to now, only ferrocenium salts with bulky counterions such as  $AlCl_4^-$ ,  $GaCl_4^-$ ,  $FeCl_4^-$ ,  $FeBr_4^-$ ,  $PF_6^-$ ,  $SbCl_4^-$ ,  $SbF_6^-$ , had been characterized by X-ray crystallography [4–10]. The cyclopentadiene rings in those ferrocenium compounds have various conformations (staggered, gauche or eclipsed) which usually change with temperature. The structures of ferrocenium salts normally exhibit a staggered conformation at high and an eclipsed conformation of the cyclopentadiene rings at low temperature (e.g.  $[FeCp_2][FeCl_4]$ ) [5,11]. In contrast to that,  $[FeCp_2][PF_6]$  reveals a phase change from a staggered disordered to an eclipsed conformation of the cyclopentadiene rings at high temperature [9]. It is interesting to note that the structure of solvent-free ferrocenium salts  $[FeCp_2][ECl_4]$  ( $E = Al, Ga, Fe$ ) is isomorphous.

The purpose of this paper is to investigate the reactivity of ferrocene towards  $AlBr_3$  and to give more information about the structures of ferrocenium salts of the type  $[FeCp_2][EX_4]$ . We herein report the solvent-free structure of  $[FeCp_2][BF_4]$ . In the presence of benzene, cocrystals of benzene and the ferrocenium complexes  $[FeCp_2][ECl_4]$  ( $E = Al, Ga$ ) have been isolated. The structure of

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$[(C_6H_6)FeCp][AlBr_4] \cdot C_6H_6$  was found to be isomorphous with those of benzene solvated  $[FeCp_2][ECl_4]$  ( $E = Al, Ga$ ).

## 2. Experimental

### 2.1. General considerations

All experiments were carried out under dry argon or nitrogen using standard Schlenk techniques. Benzene and tetrahydrofuran were distilled from sodium/benzophenone.  $CH_2Cl_2$  was dried over molecular sieves and stored under dry nitrogen.

### 2.2. Synthesis of ferrocenium tetrafluoroborate

#### $[FeCp_2][BF_4]$

Ferrocene (1.8 mmol, 0.35 g) was dissolved in 10 ml of tetrahydrofuran and a solution of  $AgBF_4$  (1.6 mmol, 0.32 g) in 10 ml tetrahydrofuran was added at  $-78^\circ C$ . The formation of a silver mirror was observed immediately. After filtration the solvent was evaporated *in vacuo*. Then the residue was extracted in 7 ml  $CH_2Cl_2$ . X-ray suitable single crystals of ferrocenium tetrafluoroborate were obtained from this solution at ambient temperature (0.40 g, 87%).

### 2.3. Synthesis of ferrocenium tetrachloroaluminate

#### $[FeCp_2][AlCl_4]$

A solution of  $Cl_2$  (2.0 mmol) in  $CH_2Cl_2$  (10 ml) was added dropwise under stirring to a slurry of ferrocene (1.8 mmol, 0.34 g) and  $AlCl_3$  (1.7 mmol, 0.23 g) in  $CH_2Cl_2$  (10 ml). After stirring for 8 h, the precipitate was removed by filtration and the solvent was evaporated *in vacuo*. Then the residue was extracted in 10 ml of benzene. X-ray suitable single crystals of ferrocenium tetrachloroaluminate were obtained from this solution at ambient temperature (0.61 g, 82%).

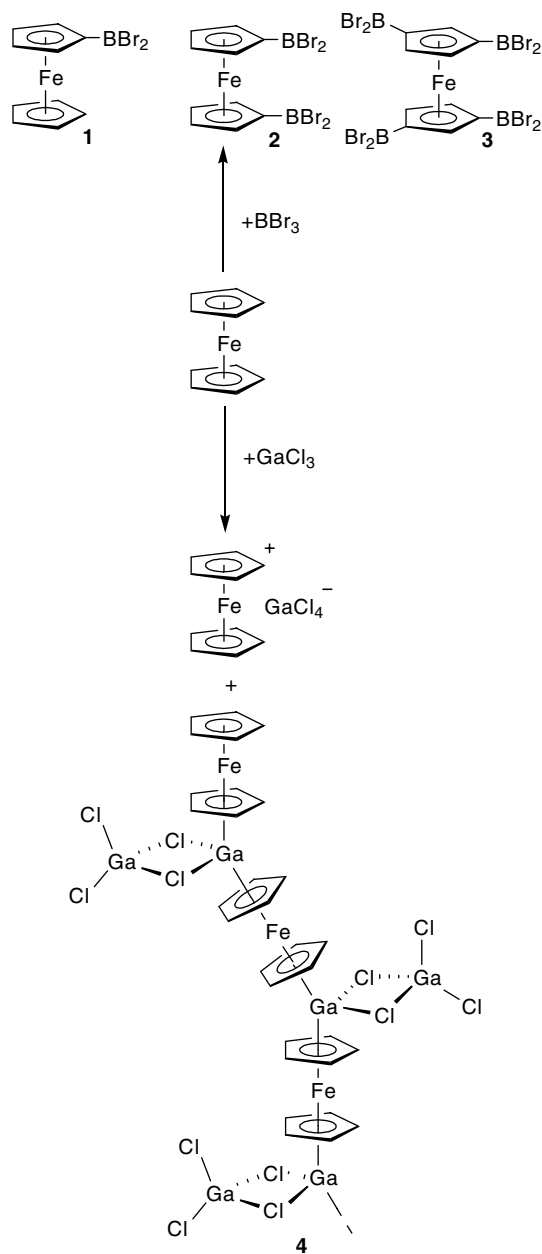
### 2.4. Synthesis of ferrocenium tetrachlorogallate

#### $[FeCp_2][GaCl_4]$

Ferrocene (1.8 mmol, 0.34 g) was dissolved in 10 ml of benzene and a solution of  $GaCl_3$  (2.5 mmol, 0.45 g) was added dropwise at ambient temperature. The solution became cloudy immediately. After 12 h at ambient temperature, X-ray suitable single crystals of  $[FeCp_2][GaCl_4] \cdot C_6H_6$  were obtained (0.76 g, 88%).

### 2.5. Synthesis of $[(C_6H_6)FeCp][AlBr_4] \cdot C_6H_6$

A mixture of ferrocene (0.5 mmol, 0.09 g) and  $AlBr_3$  (1.0 mmol, 0.26 g) in 5 ml of benzene was heated in a sealed tube for 2 h of  $120^\circ C$ . After cooling to ambient temperature, crystals of  $[(C_6H_6)FeCp][AlBr_4] \cdot C_6H_6$  were obtained (0.22 g, 70%). In the NMR spectra of the reaction solution signals of Cp-containing substances such as, among others,



Scheme 1. Reactivity of  $BBr_3$  and  $GaCl_3$  towards ferrocene.

$AlCp_3$ , cyclopentadiene and cyclopentadiene dimer were detected.

Dibromoborylferrocene (0.3 mmol, 0.11 g) was dissolved in 0.8 ml of benzene and  $AlBr_3$  (0.03 mmol, 0.08 g) was added at ambient temperature. After 12 h at ambient temperature, X-ray suitable single crystals of  $[(C_6H_6)FeCp][AlBr_4] \cdot C_6H_6$  were obtained from the reaction solution.

$[(C_6H_6)FeCp][AlBr_4] \cdot C_6H_6$ :  $^1H$  NMR ( $CD_2Cl_2$ ):  $\delta$  5.39 (s, Cp) 7.41 (s,  $C_6H_6$ ).

### 2.6. Crystal structure determination

Suitable single crystals of  $[FeCp_2][BF_4]$ ,  $[FeCp_2][ECl_4] \cdot C_6H_6$  ( $E = Al, Ga$ ) and  $[(C_6H_6)FeCp][AlBr_4] \cdot C_6H_6$  were selected and attached in a perfluoropoly-

Table 1  
Crystal data and structure refinement for  $[\text{FeCp}_2][\text{BF}_4]$ ,  $[\text{FeCp}_2][\text{AlCl}_4] \cdot \text{C}_6\text{H}_6$ ,  $[\text{FeCp}_2][\text{GaCl}_4] \cdot \text{C}_6\text{H}_6$ , and  $[(\text{C}_6\text{H}_6)\text{FeCp}][\text{AlBr}_4] \cdot \text{C}_6\text{H}_6$

	$[\text{FeCp}_2][\text{BF}_4]$	$[\text{FeCp}_2][\text{AlCl}_4] \cdot \text{C}_6\text{H}_6$	$[\text{FeCp}_2][\text{GaCl}_4] \cdot \text{C}_6\text{H}_6$	$[(\text{C}_6\text{H}_6)\text{FeCp}][\text{AlBr}_4] \cdot \text{C}_6\text{H}_6$
Formula	$\text{C}_{10}\text{H}_{10}\text{BF}_4\text{Fe}$	$\text{C}_{16}\text{H}_{16}\text{AlCl}_4\text{Fe}$	$\text{C}_{16}\text{H}_{16}\text{Cl}_4\text{FeGa}$	$\text{C}_{17}\text{H}_{17}\text{AlBr}_4\text{Fe}$
$F_w$	272.84	432.92	475.66	623.78
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	<i>Cccm</i>	<i>Cc</i>	<i>Cc</i>	<i>Cc</i>
Temperature (K)	173(2)	100(2)	173(2)	173(2)
Radiation (MoK $\alpha$ ) ( $\text{\AA}$ )	0.71073	0.71073	0.71073	0.71073
$a$ ( $\text{\AA}$ )	7.524(2)	11.8318(10)	11.8120(10)	11.9314(8)
$b$ ( $\text{\AA}$ )	11.954(4)	15.0759(14)	15.1740(10)	15.7460(10)
$c$ ( $\text{\AA}$ )	12.346(4)	11.1965(10)	11.2130(10)	11.6751(7)
$\alpha$ ( $^\circ$ )	90	90	90	90
$\beta$ ( $^\circ$ )	90	106.754(7)	106.293(6)	108.378(5)
$\gamma$ ( $^\circ$ )	90	90	90	90
$V$ ( $\text{\AA}^3$ )	1110.4(6)	1912.4(3)	1929.1(3)	2081.6(2)
$Z$	4	4	4	4
$D_{\text{calc}}$ ( $\text{Mg/m}^{-3}$ )	1.632	1.504	1.638	1.990
$\mu$ ( $\text{mm}^{-1}$ )	1.377	1.386	2.695	8.441
$F(000)$	548	876	948	1192
Crystal size (mm)	$0.13 \times 0.12 \times 0.12$	$0.36 \times 0.35 \times 0.28$	$0.38 \times 0.22 \times 0.12$	$0.28 \times 0.28 \times 0.26$
$\theta$ Range for data collection ( $^\circ$ )	3.60–27.38	3.60–27.75	2.24–28.84	2.22–28.77
Index ranges	$-9 \leq h \leq 9$ , $-15 \leq k \leq 15$ , $-15 \leq l \leq 15$	$-14 \leq h \leq 15$ , $-19 \leq k \leq 19$ , $-14 \leq l \leq 14$	$-15 \leq h \leq 15$ , $-19 \leq k \leq 19$ , $-14 \leq l \leq 13$	$-15 \leq h \leq 15$ , $-19 \leq k \leq 20$ , $-15 \leq l \leq 15$
Number of reflections collected	3224	13030	13758	17327
Number of independent reflections	663	4235	3732	4670
$R_{\text{int}}$	0.0627	0.0478	0.0389	0.0400
Completeness to $\theta = 24.76^\circ$ (%)	99.1	98.9	89.1	89.9
Absorption correction	empirical	semi-empirical from equivalents	empirical	empirical
Maximum and minimum transmission	0.8521 and 0.8412	0.6976 and 0.6353	0.7381 and 0.4274	0.2176 and 0.2009
Refinement method	full-matrix least-squares on $F^2$	full-matrix least-squares on $F^2$	full-matrix least-squares on $F^2$	full-matrix least-squares on $F^2$
Data/restraints/parameters	663/0/41	4235/2/200	3732/2/199	4670/24/205
Goodness-of-fit on $F^2$	1.027	1.027	1.089	1.042
$R_1$ , $wR_2$ ( $I > 2\sigma(I)$ )	0.0518, 0.1283	0.0684, 0.1759	0.0318, 0.0609	0.0444, 0.0823
$R_1$ , $wR_2$ (all data)	0.1034, 0.1533	0.0718, 0.1811	0.0397, 0.0635	0.0669, 0.0909
Absolute structure parameter		0.70(3)	0.091(12)	0.127(16)
Largest difference in peak and hole ( $\text{e \AA}^{-3}$ )	0.176 and $-0.583$	1.587 and $-1.308$	0.429 and $-0.331$	0.660 and $-0.505$
CCDC	632409	632410	170257	632408

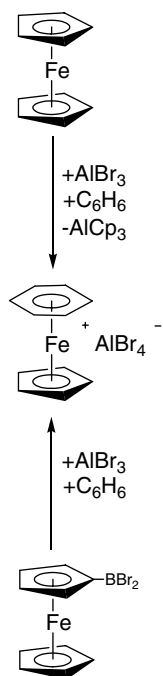
ther oil to a thin glass fiber. Intensity measurement was carried out using a STOE IPDS-II two circle diffractometer. The structures were solved with direct methods [12] and refined with full-matrix least-squares techniques [13]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions and refined using a riding model. Crystal data, data collection parameters, and refinement statistics for  $[\text{FeCp}_2][\text{BF}_4]$ ,  $[\text{FeCp}_2][\text{ECl}_4]$  ( $\text{E} = \text{Al}, \text{Ga}$ ) and  $[(\text{C}_6\text{H}_6)\text{FeCp}][\text{AlBr}_4] \cdot \text{C}_6\text{H}_6$  are listed in Table 1.

### 3. Results and discussion

#### 3.1. Reaction of ferrocene with $\text{AlBr}_3$

To date, several procedures for the preparation of  $\text{Fe}^{2+}$ -arene cation of type  $[(\text{arene})\text{FeCp}]^+$  have been

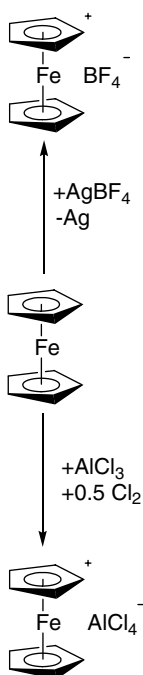
described in the literature [14,15]. The most common methods are the reactions of  $\text{Al}/\text{AlCl}_3$  mixtures and aromatic compounds with  $\text{CpFe}(\text{CO})\text{Br}$  or ferrocene. Now we have found a facile route to the  $\text{Fe}^{2+}$ -arene complex  $[(\text{C}_6\text{H}_6)\text{FeCp}][\text{AlBr}_4]$  by the reaction of ferrocene with benzene in the presence of  $\text{AlBr}_3$  at  $120^\circ\text{C}$  (Scheme 2). Single crystals of  $[(\text{C}_6\text{H}_6)\text{FeCp}][\text{AlBr}_4]$ , suitable for X-ray diffraction, were grown from the reaction solution at ambient temperature. In the NMR spectra of the reaction solution signals of Cp-containing substances such as, among others,  $\text{AlCp}_3$ , cyclopentadiene and cyclopentadiene dimer were detected. It is interesting to note that treatment of dibromoborylferrocene with  $\text{AlBr}_3$  in benzene also leads to the formation of  $[(\text{C}_6\text{H}_6)\text{FeCp}][\text{AlBr}_4]$  (Scheme 2). Several studies have revealed that  $\text{Fe}^{2+}$ -arene complexes of the type  $[(\text{C}_6\text{H}_6)\text{FeCp}]^+$  are convenient sources for  $\text{Fe}(\text{I})$  complexes [16].



Scheme 2. Routes to the  $\text{Fe}^{2+}$ -arene complex  $[(\text{C}_6\text{H}_6)\text{FeCp}][\text{AlBr}_4]$  by the reaction of ferrocene and dibromoborylferrocene with  $\text{AlBr}_3$ .

### 3.2. Syntheses of ferrocenium complexes of type $[\text{FeCp}_2][\text{BF}_4]$

Oxidation of ferrocene with silver(I) salts is a common route to ferrocenium cations, and this method was used, as shown in Scheme 3, to prepare  $[\text{FeCp}_2][\text{BF}_4]$



Scheme 3. Syntheses of the ferrocenium complexes  $[\text{FeCp}_2][\text{BF}_4]$  and  $[\text{FeCp}_2][\text{AlCl}_4]$ .

for this study. The synthesis of  $[\text{FeCp}_2][\text{AlCl}_4]$ , however, was achieved by the reaction of ferrocene with  $\text{Cl}_2$  in  $\text{CH}_2\text{Cl}_2$  in the presence of  $\text{AlCl}_3$  at ambient temperature (Scheme 3). Recrystallization from benzene yields blue-green blocks of  $[\text{FeCp}_2][\text{AlCl}_4]$  as benzene solvate. On the hand, side X-ray quality crystals of the ferrocenium salt  $[\text{FeCp}_2][\text{GaCl}_4] \cdot \text{C}_6\text{H}_6$  were accessible from the reaction of  $\text{GaCl}_3$  and ferrocene in benzene (Scheme 1).

### 3.3. X-ray crystallographic structures

The molecular structures of complexes  $[\text{FeCp}_2][\text{BF}_4]$ ,  $[\text{FeCp}_2][\text{AlCl}_4] \cdot \text{C}_6\text{H}_6$ ,  $[\text{FeCp}_2][\text{GaCl}_4] \cdot \text{C}_6\text{H}_6$ , and  $[(\text{C}_6\text{H}_6)\text{FeCp}][\text{AlBr}_4] \cdot \text{C}_6\text{H}_6$  are shown in Figs. 1–6.

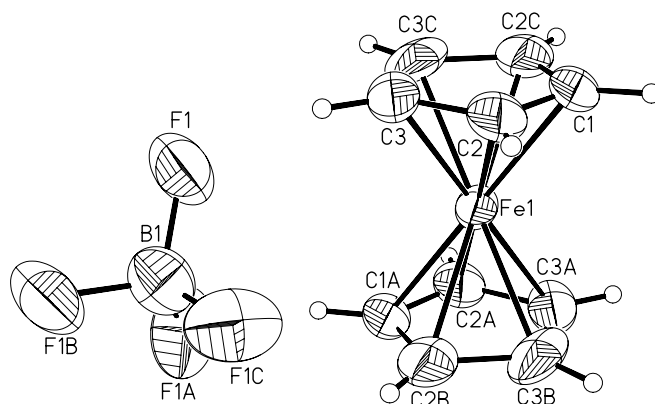


Fig. 1. ORTEP plot of  $[\text{FeCp}_2][\text{BF}_4]$  in the solid state. Displacement ellipsoids are drawn at the 50% probability level.

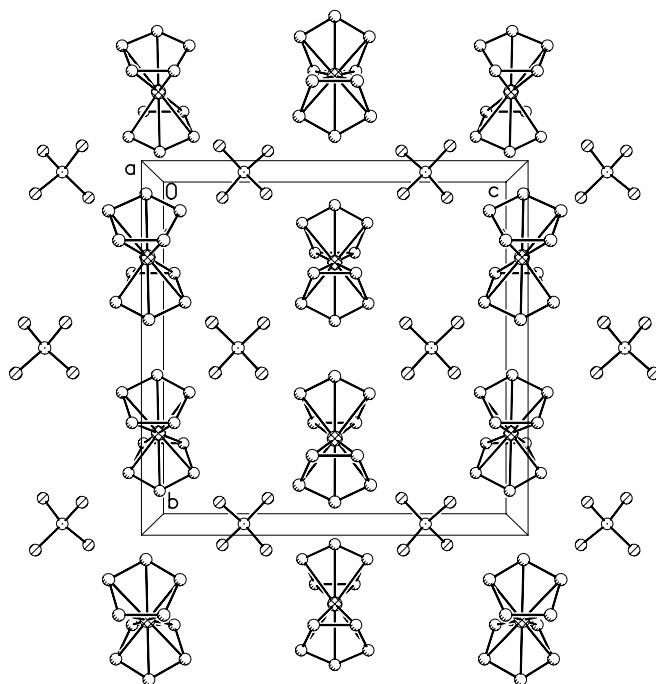


Fig. 2. Crystal packing diagram for  $[\text{FeCp}_2][\text{BF}_4]$ .

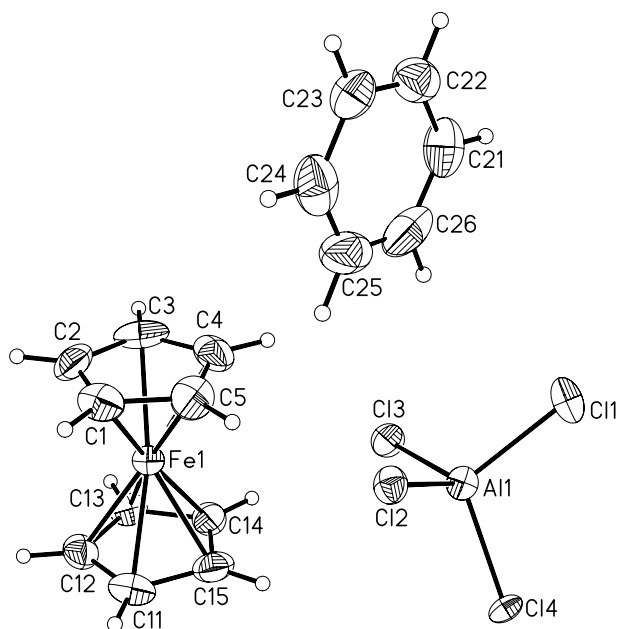


Fig. 3. ORTEP plot of  $[\text{FeCp}_2][\text{AlCl}_4]$  with one molecule  $\text{C}_6\text{H}_6$  in the solid state. Displacement ellipsoids are drawn at the 50% probability level.

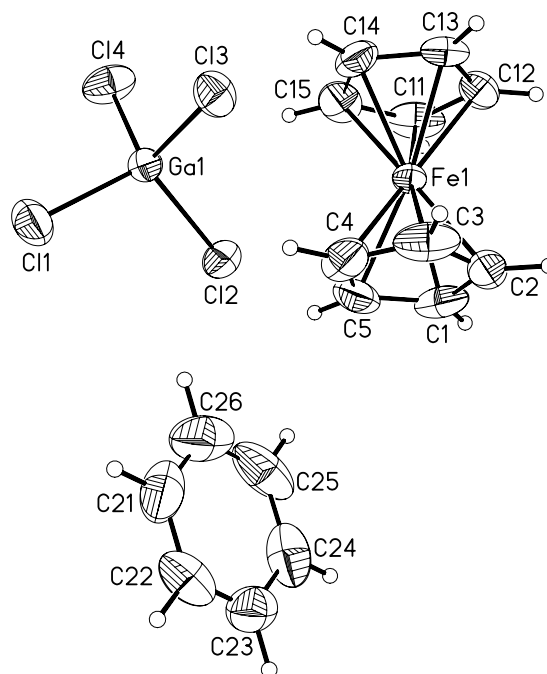


Fig. 5. ORTEP plot of  $[\text{FeCp}_2][\text{GaCl}_4]$  with one molecule  $\text{C}_6\text{H}_6$  in the solid state. Displacement ellipsoids are drawn at the 50% probability level.

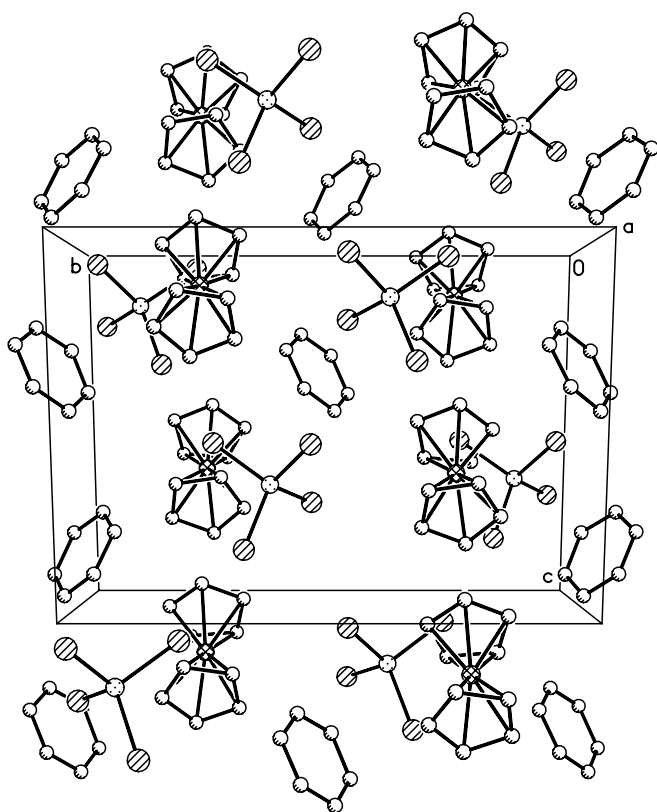


Fig. 4. Crystal packing diagram for  $[\text{FeCp}_2][\text{AlCl}_4] \cdot \text{C}_6\text{H}_6$ .

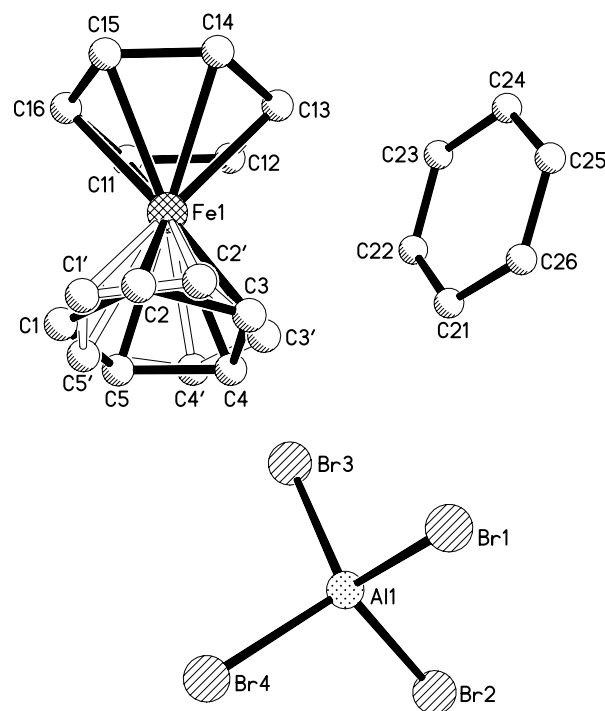


Fig. 6. Plot of  $[(\text{C}_6\text{H}_6)\text{FeCp}][\text{AlBr}_4]$  with one molecule  $\text{C}_6\text{H}_6$  in the solid state. The cyclopentadienyl ligand of  $[(\text{C}_6\text{H}_6)\text{FeCp}]$  cation is disordered over two positions.

We obtained single crystals of  $[\text{FeCp}_2][\text{BF}_4]$ , which are free of solvent, from  $\text{CH}_2\text{Cl}_2$  at ambient temperature. Crystallization from benzene at ambient temperature yields

X-ray quality crystals of  $[\text{FeCp}_2][\text{GaCl}_4] \cdot \text{C}_6\text{H}_6$  and  $[\text{FeCp}_2][\text{AlCl}_4] \cdot \text{C}_6\text{H}_6$ , respectively. Single crystals of  $[(\text{C}_6\text{H}_6)\text{FeCp}][\text{AlBr}_4] \cdot \text{C}_6\text{H}_6$ , suitable for X-ray diffraction, were

also grown from a benzene solution at ambient temperature.

X-ray structure analyses of the solvent-free ferrocenium compounds  $[\text{FeCp}_2][\text{ECl}_4]$  ( $\text{E} = \text{Al}, \text{Ga}, \text{Fe}$ ) reveal that all of them crystallize in orthorhombic space group  $Pnma$  [4,5]. However, the cell parameters of solvent-free ferrocenium tetrafluoroborate are quite different from those of  $[\text{FeCp}_2][\text{ECl}_4]$  ( $\text{E} = \text{Al}, \text{Ga}, \text{Fe}$ ). The cell dimensions of  $[\text{FeCp}_2][\text{BF}_4]$  are  $a = 7.524(2) \text{ \AA}$ ,  $b = 11.954(4) \text{ \AA}$ ,  $c =$

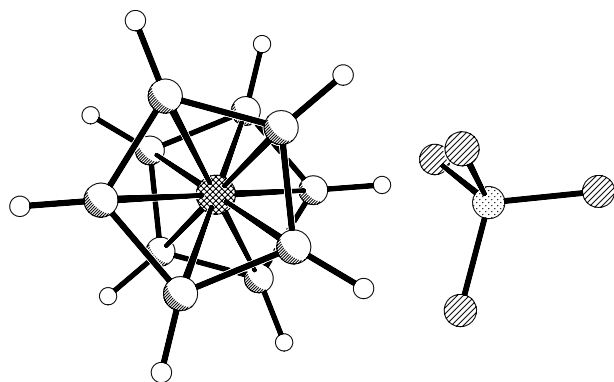


Fig. 7. Cp ligand rotation of  $[\text{FeCp}_2][\text{BF}_4]$  away from the eclipsed conformation.

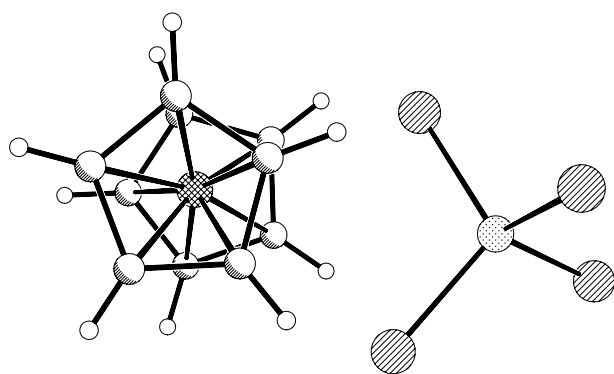


Fig. 8. Cp ligand rotation of  $[\text{FeCp}_2][\text{AlCl}_4] \cdot \text{C}_6\text{H}_6$  away from the eclipsed conformation.

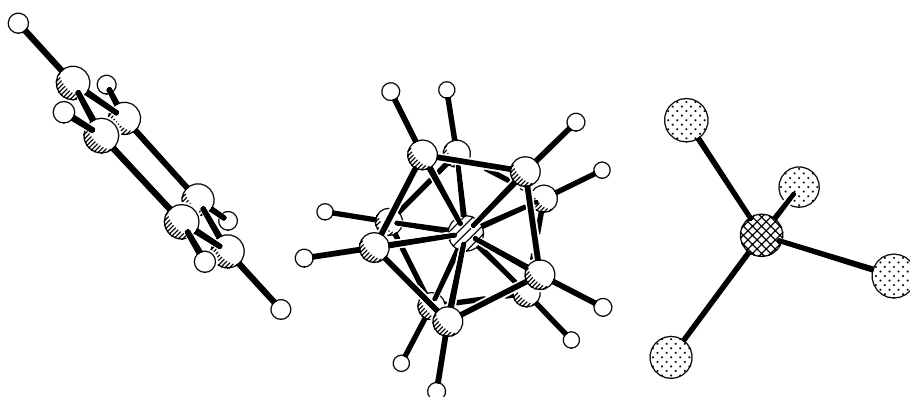


Fig. 9. Cp ligand rotation of  $[\text{FeCp}_2][\text{GaCl}_4] \cdot \text{C}_6\text{H}_6$  away from the eclipsed conformation.

$12.346(4) \text{ \AA}$  and  $\alpha = \beta = \gamma = 90^\circ$ . The structural parameters of cocrystals of benzene and the ferrocenium complexes  $[\text{FeCp}_2][\text{ECl}_4]$  ( $\text{E} = \text{Al}, \text{Ga}$ ), which crystallize in the monoclinic space group  $Cc$ , are similar to those of the cobaltocenium derivative  $[\text{CoCp}_2][\text{GaCl}_4] \cdot \text{C}_6\text{H}_6$  [4]. Therefore, these ferrocenium compounds are isomorphous with the cobaltocenium complex  $[\text{CoCp}_2][\text{GaCl}_4] \cdot \text{C}_6\text{H}_6$ . Surprisingly, the structure of the  $\text{Fe}^{2+}$ -arene complex  $[(\text{C}_6\text{H}_6)\text{FeCp}][\text{AlBr}_4] \cdot \text{C}_6\text{H}_6$  was found to be isomorphous with those of  $[\text{FeCp}_2][\text{ECl}_4] \cdot \text{C}_6\text{H}_6$  ( $\text{E} = \text{Al}, \text{Ga}$ ) and  $[\text{CoCp}_2][\text{GaCl}_4] \cdot \text{C}_6\text{H}_6$  as well. The complex  $[(\text{C}_6\text{H}_6)\text{FeCp}][\text{AlBr}_4] \cdot \text{C}_6\text{H}_6$  reveals a structure in which the cyclopentadienyl ligand of the  $[(\text{C}_6\text{H}_6)\text{FeCp}]$  cation is disordered over two positions, which have an occupancy ratio of roughly 1:1.

The ferrocenium salts listed in Table 1 possess quite similar Fe–C bond lengths in the solid (range of 2.064 Å for  $[\text{FeCp}_2][\text{AlCl}_4]$  and 2.095 Å for  $[\text{FeCp}_2][\text{BF}_4]$ ). The average values for the C–C bonds of Cp rings of these ferrocenium complexes are found to be between 1.385 Å for  $[\text{FeCp}_2][\text{AlCl}_4]$  to 1.417 Å for  $[\text{FeCp}_2][\text{BF}_4]$  and are therefore comparable with those of ferrocene.

The Fe–CG<sub>Cp</sub> (CG: center of gravity) distances found of the ferrocenium salts  $[\text{FeCp}_2][\text{BF}_4]$  and  $[\text{FeCp}_2][\text{ECl}_4] \cdot \text{C}_6\text{H}_6$  ( $\text{E} = \text{Al}, \text{Ga}$ ) range between 1.691 Å  $\{[\text{FeCp}_2][\text{GaCl}_4]\}$  and 1.711 Å  $\{[\text{FeCp}_2][\text{BF}_4]\}$ , whereas the structure of  $[(\text{C}_6\text{H}_6)\text{FeCp}][\text{AlBr}_4]$  features the Fe–CG<sub>benzene</sub> distance of 1.529 Å and Fe–CG<sub>Cp</sub> distance of 1.637 Å, respectively. The shorter Fe(II) arene contacts in  $[(\text{C}_6\text{H}_6)\text{FeCp}][\text{AlBr}_4]$  are the result of stronger  $\pi$  interactions of Fe(II) with arenes than those of Fe(III) in ferrocenium compounds.

In contrast to the Cp rings of solvent-free  $[\text{FeCp}_2][\text{ECl}_4]$  ( $\text{E} = \text{Al}, \text{Ga}, \text{Fe}$ ) the Cp ligands of  $[\text{FeCp}_2][\text{BF}_4]$ ,  $[\text{FeCp}_2][\text{ECl}_4] \cdot \text{C}_6\text{H}_6$ , ( $\text{E} = \text{Al}, \text{Ga}$ ) and  $[\text{CoCp}_2][\text{GaCl}_4] \cdot \text{C}_6\text{H}_6$  are rotated away from the eclipsed conformation, as shown in Figs. 7–9.

#### 4. Supplementary material

CCDC 632409, 632410, 170257 and 632408 contain the supplementary crystallographic data for  $\{[\text{FeCp}_2][\text{BF}_4]\}$ ,

{[FeCp<sub>2</sub>][AlCl<sub>4</sub>]·C<sub>6</sub>H<sub>6</sub>}, {[FeCp<sub>2</sub>][GaCl<sub>4</sub>]·C<sub>6</sub>H<sub>6</sub>} and {[C<sub>6</sub>H<sub>6</sub>FeCp][AlBr<sub>4</sub>]·C<sub>6</sub>H<sub>6</sub>}. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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