Molecular structure of iodo [1.1]ferrocenylruthenocenophanium$^+$ BF$_4^-$ salt

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Abstract

The structure of iodo[1.1]ferrocenylruthenocenophanium$^+$ BF$_4^-$ (1), prepared by oxidation of [1.1]ferrocenylruthenocenophane ([1.1]FcRc) with iodoruthenocenium$^+$BF$_4^-$ ([RcHI]$^+$BF$_4^-$) was analyzed by single-crystal X-ray diffraction. The crystal form of 1 is triclinic, space group $P\bar{1}$, $a = 9.794(2)$, $b = 14.393(4)$, $c = 7.777(2)$ Å, $\alpha = 101.62(4)$, $\beta = 93.17(4)$, $\gamma = 72.09(2)°$, $Z = 2$, and the final R and R_w were both 0.052. The cation exists in a *syn*-conformation, as with other [1.1]metallocenophanes, and is given the formula [Fe(II)(C$_5$H$_4$CH$_2$C$_5$H$_4$)$_2$Ru(IV)I]$^+$ with Ru(IV)–I bond (2.751(1) Å) formation in the solid. The distance between the Ru(IV) and Fe(II) atoms is 4.719(1) Å, which is slightly shorter than the value for [1.1]FcRc, and the bond angle of I–Ru(IV)–Fe(II) is 91.50(1)°. The cation has two kinds of twisted C$_5$H$_4$CH$_2$C$_5$H$_4$ systems. The cyclopentadienyl rings in the [Cp(C$_5$H$_4$)RuI]$^+$ moiety are highly slanted (the dihedral angle between the Cp ring and fulvenide ligand is 33.87°) owing to the Ru(IV)–I bond. Large downfield shifts of the ^{13}C CP/MAS NMR signals for the ruthenocene moiety are explained by the same fact.

Keywords: Iron; Ruthenium; Metallocenes

1. Introduction

Although a large number of structural studies of mixed valence biferrocenium salts have been reported, no structural studies of mixed valence biruthenocenium salts have so far been published except for crystal structural studies on the mixed valence iodobiruthenocenium(II,IV) tetrafluoroborate salt, [Ru(II)Cp(C$_5$H$_4$)-(C$_5$H$_4$)CpRu(IV)]$^+$ BF$_4^-$ (abbreviated as [RcRcI]$^+$BF$_4^-$) by the present authors [1]. The two Cp rings are transoid with respect to the fulvalene ligand. The Ru(II)- - -Ru(IV) distance is 5.464(4) Å, which indicates that there is no direct interaction between them. The most interesting results in the studies are an extraordinarily large dihedral angle (42.4°) between Cp and the fulvenide ligand on the Ru(IV) side (the angle is 32.2° for iodoruthenocenium(IV) triiodide [2]) and the nonplanarity of both the fulvenide ligand (C$_5$H$_4$C$_5$H$_4$) and the C$_5$H$_4$ group in the ruthenocenium(Ru(IV)) moiety.

These phenomena are due to the repulsion between I and the two C$_1$ atoms which connect the two C$_5$H$_4$ moieties in the fulvenide.

The other interesting binuclear metallocene is [1.1]FcRc (prepared by reduction of [1.1]ferrocenyl-ruthenocenophane-1,13-dione with AlCl$_3$–LiAlH$_4$ [3]) in which the central metal atoms (Fe(II), Ru(II)) exist in a *syn*-conformation. Therefore, some interaction between them in its salts may be expected as in the case of the dicationic [1.1]ruthenocenophanium^{2+} (BF$_4^-$)$_2$ salt (with intramolecular bond formation between the two Ru(III) atoms, 2.951(1) Å) reported by Mueller-Westerhoff et al. [4].

Cyclic voltammograms of [1.1]FcRc reported by Diaz et al. [5] show two independent peaks; one is a quasi-reversible one-electron oxidation peak (Fe(II) to Fe(III)) at 0.40 V, and the other is an irreversible two-electron oxidation peak at 0.94 V (Ru(II) to Ru(IV)); i.e. [1.1]FcRc can be oxidized easily to give monocationic ferrocenium salts by using appropriate oxidizing agents. In the present studies, [1.1]FcRc was oxidized by [RcHI]$^+$BF$_4^-$ giving deep brown precipitates. Contrary

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to our expectations, the main oxidized product was found not to be a monocationic ferrocenium salt ([1.1]FcRc$^+$BF$_4^-$ formulated as [Fe(III)(C$_5$H$_4$CH$_2$-C$_5$H$_4$)$_2$Ru(II)]$^+$BF$_4^-$) but a dicationic salt **1**. The present study was carried out to investigate the crystal structure of **1** in comparison with that of neutral [1.1]FcRc reported by Rheingold et al. [6], and to investigate the chemical state of the Fe and Ru atoms in the solid by mean of ^{13}C-CP/MAS NMR spectroscopy.

2. Experimental

2.1. Syntheses

Salt **1** was prepared as follows: [1.1]FcRc (100 mg, 0.227 mmol) dissolved in CH$_2$Cl$_2$ (50 cm^3) was added to a stoichiometric amount of [RcHI]$^+$BF$_4^-$ (101 mg, 0.227 mmol) dissolved in CH$_2$Cl$_2$ (100 cm^3). The mixture was stirred for 1 h and the solvent was evaporated. After extraction of RcH with benzene, **1** was obtained by recrystallization from a CH$_2$Cl$_2$–C$_6$H$_{14}$ mixture as deep purple crystals (125 mg; yield 84%). Single crystals suitable for X-ray studies were obtained by diffusion of hexane vapor into a CH$_2$Cl$_2$ solution of **1** at room temperature. Found: C, 40.31; H, 3.22. C$_{22}$H$_{20}$BF$_4$FeIRu calc.; C, 40.34; H, 3.08%.

2.2. Measurements

^{13}C CP/MAS NMR spectra were recorded on a JEOL EX-270 NMR spectrometer operating at 67.8 MHz with a CP/MAS accessory. Samples (ca. 100 mg) were contained in a cylindrical rotor made of zirconia and spun at a speed of up to 5.8–6.2 kHz. Contact time was 5 ms, and repetition time 5 s. Spectral width and data points were 27 kHz and 8 kHz, respectively. Spectra were usually accumulated 400–2000 times to achieve reasonable S/N ratios. The ^{13}C NMR chemical shifts were calibrated indirectly through external adamantane (29.5 ppm relative to tetramethylsilane). In the dipolar dephasing experiments, the ^{13}C dipolar dephasing time was determined by measuring the ^{13}C-Cp/MAS NMR spectra, varying the delay time, τ, for the proton dipolar decoupling and obtaining data in the range 10–60 μs. The delay time for proton decoupling and data acquisition in this experiment was 20 μs, which was long enough to eliminate the ^{13}C-signals of all protonated carbons except for methyl carbons.

2.3. X-ray crystallography

A deep purple plate having approximate dimensions 0.3 × 0.2 × 0.04 mm^3 was selected. X-ray diffraction experiments were carried out on a Rigaku AFC-6A automated four-circle X-ray diffractometer with graphite

monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å). The lattice parameters were determined by a least-squares calculation with 25 reflections. Crystal data for **1** at 298 K were triclinic, space group $P\bar{1}$, $a = 9.794(2)$, $b = 14.393(4)$, $c = 7.777(2)$ Å, $\alpha = 101.62(4)$, $\beta = 93.17(4)$, $\gamma = 72.09(2)°$, $Z = 2$ and the final discrepancy factors R and R_w were both 0.052. Crystal stability was checked by recording three standard reflections for every 200, and no significant variations were observed; 6764 independent reflections were measured, of which 5434 were observed with [$|F_0| > 3\sigma(F_0)$]. Intensity data were collected over the range $4° \leq 2\theta \leq 60°$ using the 2θ–ω scan mode with scanning speed 4° min^{-1}, and the range of indices was $-12 \leq h \leq 12, -18 \leq l \leq 18, 0 \leq k \leq 10$. The reflection data were corrected for Lorentz and polarization factors and for absorption [7] but not for extinction.

The structure of **1** was solved by heavy-atom methods. Positions of the metal (Ru, Fe) and iodine atoms were deduced from the three-dimensional Patterson map, other atoms (C, B, F) being located by successive Fourier syntheses. Their positional and thermal parameters were refined by block-diagonal least-squares methods. The thermal motions of nonhydrogen atoms were refined anisotropically. Positions of hydrogen atoms were deduced from difference Fourier syntheses. Atomic-scattering factors for nonhydrogen and hydrogen atoms were taken from refs. [8] and [9], respectively. All calculations were carried out on a FACOM FMR60 computer at the Educational Computer Center of the University of Tokyo, using a local version of the UNICS-III program [10]. Crystallographic data of **1** and some experimental conditions for the X-ray structure analysis are listed in Table 1.

3. Results and discussion

The final atomic coordinates and equivalent isotropic temperature factors (B_{eq}) of nonhydrogen atoms, interatomic distances, and bond and dihedral angles for **1** are shown in Tables 2–5, and ORTEP drawings of the cation with the atom numbering system are shown in Fig. 1; The cation exists in a *syn*-conformation, as with neutral [1.1]FcRc. The distance between the Fe(1) and Ru(1) atoms was found to be 4.719(1) Å, suggesting no bond formation between them. The iodine atom is coordinated to the Ru atom from the opposite side of methylene group, probably avoiding the steric hindrance between -CH$_2$- and I. The bond angle of I–Ru(1)–Fe(1) is 91.50(1)°. The Ru–I distance (2.751(1) Å) is slightly longer than the distance reported for Ru(IV)–I in [RcRcI]$^+$ (2.717(2) Å) and [RcHI]$^+$ (2.732(3) Å) [1,2].

The distance from I to C(12), C(13), C(17) and C(18) were found to be 3.322(7), 3.122(8), 3.153(7) and 3.274(7) Å, respectively. These values are much shorter

Table 1
Crystal data for **1**

Formula	$C_{22}H_{20}BF_4FeIRu$
Formula weight	655.03
Space group	$P\bar{1}$
a/Å	9.794(2)
b/Å	14.393(4)
c/Å	7.777(2)
α/°	101.62(4)
β/°	93.17(4)
γ/°	72.09(2)
V/Å^3	1021(1)
Z	2
Dx/g cm^{-3}	2.13
T/°C	22
λ/Å	0.71073
μ/cm^{-1}	13.41
No. of reflections measured	6764
No. of reflections with $|Fo| > 3\sigma(Fo)$	5434
R [a]	0.052
R_w [b]	0.052

[a] $R_w = \Sigma \|Fo| - |Fc\| / \Sigma |Fo|$.

[b] $R_w = (\Sigma\omega(\|Fo| - |Fc\|^2 / \Sigma\omega(|Fo|^2))^{1/2}$. $\omega = 0.5$ for $|Fo| < 30.0$;

$\omega = 1.0$ for $30.0 \leqslant |Fo| \leqslant 50.0$; $\omega = 2500/|Fo|^2$ for $50 < |Fo|$.

Table 2
Atomic coordinates ($\times 10^4$) and isotropic temperature factors

Atom	x	y	z	B_{eq} [a] /Å^2
Fe	7804.5(8)	4352.6(5)	6367.9(1)	2.5
Ru	6299.6(5)	1585.0(3)	6747.2(6)	2.5
I	3856.4(6)	2271.6(4)	4873.5(9)	5.7
C(1)	7763(7)	4064(4)	8844(7)	3.1
C(2)	6527(7)	4843(4)	8560(7)	3.4
C(3)	6971(9)	5634(5)	8175(8)	4.3
C(4)	8465(9)	5348(5)	8204(8)	4.6
C(5)	8976(8)	4385(5)	8618(8)	4.0
C(6)	8402(6)	3036(4)	4570(7)	2.7
C(7)	6927(6)	3549(4)	4381(7)	2.8
C(8)	6818(6)	4499(4)	4005(8)	3.3
C(9)	8225(7)	4574(4)	3953(7)	3.3
C(10)	9196(6)	3674(4)	4309(7)	3.1
C(11)	6748(7)	2630(4)	9139(7)	3.1
C(12)	5312(7)	2967(4)	8687(9)	3.8
C(13)	4620(8)	2233(5)	8815(10)	4.6
C(14)	5638(9)	1434(5)	9340(8)	4.7
C(15)	6957(8)	1647(5)	9490(8)	4.0
C(16)	8238(6)	1353(4)	5067(8)	3.3
C(17)	7128(8)	1167(5)	4002(8)	4.0
C(18)	6743(9)	343(5)	4456(9)	4.6
C(19)	7612(8)	33(4)	5847(10)	4.6
C(20)	8531(7)	659(4)	6264(9)	3.7
C(21)	7909(7)	3115(5)	9457(7)	3.5
C(22)	9130(6)	2007(4)	4920(8)	3.5
B	1629(7)	1209(6)	−87(9)	3.3
F(1)	777(12)	755(11)	−150(26)	25.6
F(2)	1379(13)	1836(13)	1181(15)	24.8
F(3)	1376(8)	1673(9)	−1384(12)	16.8
F(4)	3025(6)	655(5)	−96(11)	10.0

[a] $B_{eq} = 4/3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{13}ac\cos\beta + B_{12}ab\cos\gamma + B_{23}bc\cos\alpha)$. B_{ij}'s are defined by $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2klB_{23} + 2hlB_{13} + 2hkB_{12})]$.

Table 3
Interatomic distances for **1**

Atom 1	Atom 2	Dist/Å	Atom 1	Atom 2	Distance/Å
Fe	Ru	4.719(1)	Fe	I	5.524(1)
Ru	I	2.751(1)	Fe	C(1)	2.055(6)
Fe	C(2)	2.044(6)	Fe	C(3)	2.049(5)
Fe	C(4)	2.037(8)	Fe	C(5)	2.039(7)
Fe	C(6)	2.057(5)	Fe	C(7)	2.051(6)
Fe	C(8)	2.046(6)	Fe	C(9)	2.051(6)
Fe	C(10)	2.043(6)	Ru	C(11)	2.259(5)
Ru	C(12)	2.223(6)	Ru	C(13)	2.216(7)
Ru	C(14)	2.223(8)	Ru	C(15)	2.186(6)
Ru	C(16)	2.266(6)	Ru	C(17)	2.226(6)
Ru	C(18)	2.211(6)	Ru	C(19)	2.199(6)
Ru	C(20)	2.190(6)	C(1)	C(2)	1.42(1)
C(2)	C(3)	1.43(1)	C(3)	C(4)	1.39(1)
C(4)	C(5)	1.42(1)	C(5)	C(1)	1.43(1)
C(6)	C(7)	1.42(7)	C(7)	C(8)	1.43(1)
C(8)	C(9)	1.42(1)	C(9)	C(10)	1.42(1)
C(10)	C(6)	1.42(1)	C(1)	C(21)	1.50(1)
C(11)	C(21)	1.49(1)	C(11)	C(12)	1.39(1)
C(12)	C(13)	1.44(1)	C(13)	C(14)	1.39(1)
C(14)	C(15)	1.41(1)	C(15)	C(11)	1.45(1)
C(16)	C(17)	1.39(1)	C(17)	C(18)	1.46(1)
C(18)	C(19)	1.40(1)	C(19)	C(20)	1.44(1)
C(20)	C(16)	1.45(1)	C(6)	C(22)	1.51(1)
C(16)	C(22)	1.49(1)	B	F(1)	1.202(18)
B	F(2)	1.174(14)	B	F(3)	1.291(14)
B	F(4)	1.354(8)	I	F(1)	5.333(16)
I	F(2)	3.737(12)	I	F(3)	5.349(9)
I	F(4)	4.267(7)			

Table 4
Bond angles (deg) for **1**

C(1)–C(2)–C(3)	108.6(6)	C(2)–C(3)–C(4)		108.0(6)
C(3)–C(4)–C(5)	108.5(8)	C(4)–C(5)–C(1)		108.5(6)
C(5)–C(1)–C(2)	106.7(6)	C(6)–C(7)–C(8)		108.3(6)
C(7)–C(8)–C(9)	108.1(5)	C(8)–C(9)–C(10)		107.5(6)
C(9)–C(10)–C(6)	108.8(5)	C(15)–C(11)–C(12)		105.3(6)
C(11)–C(12)–C(13)	109.6(6)	C(12)–C(13)–C(14)		108.0(7)
C(13)–C(14)–C(15)	107.5(7)	C(14)–C(15)–C(11)		109.6(6)
C(20)–C(16)–C(17)	105.9(6)	C(16)–C(17)–C(18)		109.8(6)
C(17)–C(18)–C(19)	107.9(7)	C(18)–C(19)–C(20)		107.1(7)
C(19)–C(20)–C(16)	109.3(6)	C(5)–C(1)–C(21)		122.3(5)
C(2)–C(1)–C(21)	130.7(6)	C(7)–C(6)–C(22)		130.9(6)
C(10)–C(6)–C(22)	121.8(5)	C(15)–C(11)–C(21)		121.5(5)
C(12)–C(11)–C(21)	132.9(6)	C(17)–C(16)–C(22)		129.3(6)
C(20)–C(16)–C(22)	124.3(5)	C(1)–C(21)–C(11)		121.0(5)
C(6)–C(22)–C(16)	119.0(5)	F(1)–B–F(2)		107.8(13)
F(1)–B–F(3)	107.8(12)	F(1)–B–F(4)		115.3(9)
F(2)–B–F(3)	105.3(11)	F(2)–B–F(4)		109.7(8)
F(3)–B–F(4)	110.3(7)			

Table 5
Dihedral angles (deg) between planes

Plane	Plane		
	C(6)–C(10)	C(11)–C(15)	C(16)–C(20)
C(1)–C(5)	2.36	11.19	43.24
C(6)–C(10)	–	9.18	42.02
C(11)–C(15)	–	–	33.87

than those for other C atoms (e.g. I–C(16) 4.089(6) Å) and are less than the sum (3.85 Å) of the van der Waals radii of C and I [11]. The results are consistent with the much larger dihedral angle (33.87°) between the rings on the Ru side compared with the angle on the Fe side (2.36°), and the value is even a little larger than that for the [RcHI]$^+$ cation (32.2°). The distance between Fe and I atoms (5.524(1) Å) shows that there is no bond formation between Fe and I. These results indicate that the oxidation states of Fe and Ru can be assigned as Fe(II) and Ru(IV), respectively, and the cation is thus given the formula [Fe(II)(H$_4$C$_5$CH$_2$C$_5$H$_4$)$_2$Ru(IV)I]$^+$ in the solid.

This assignment is unexpected from the results of cyclic voltammograms for [1.1]FcRc, i.e. the Fe was oxidized more easily than Ru giving a ferrocenium salt. The same conclusion is reported for iodoferrocenylruthenocenium salts [Fe(II)Cp(H$_4$C$_5$C$_5$H$_4$)CpRu(IV)I]$^+$Y$^-$ (Y = I$_3$, PF$_6$, BF$_4$) prepared by the oxidation of ferrocenylruthenocene with iodine or [RcHI]$^+$Y$^-$ (Y = PF$_6$, BF$_4$) [12]. These results suggest that the stability of the Ru(IV)–I bond may prevent the formation of the ferrocenium salt in the solid.

It is important to compare molecular structure parameters of the cation with the reported values for FcH,
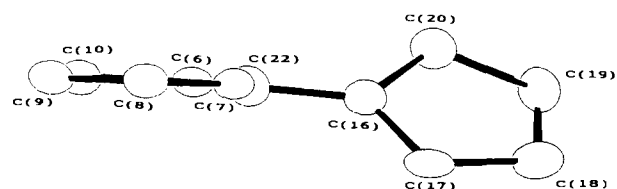

Fig. 1. ORTEP drawing of the cation of **1** with the numbering scheme of the atoms.

Fig. 2. ORTEP drawing of C$_5$H$_4$CH$_2$C$_5$H$_4$ (plane C$_6$–C$_{10}$, plane C$_{16}$–C$_{20}$).

RcH and [1.1]FcRc [5,13,14]. As shown in Fig. 1, the conformation of the Cp rings is essentially eclipsed, which is comparable with the conformation of neutral [1.1]FcRc. The average C–C length for the Cp and C$_5$H$_4$ rings in the ferrocene moiety is 1.42(1) Å, which agrees with that for the ruthenocene moiety (1.42(3) Å) and is close to those reported for FcH (1.403 ± 0.02 Å), RcH (1.43(3) Å) and [RcHI]$^+$ I$_3^-$ (1.41(3) Å).

The difference in oxidation states is due to the different metal–C bond lengths. The average distance from Fe(II) to C atoms in five-membered Cp rings (C(1)–C(10)) was found to be 2.047(6) Å, which corresponds well to that for [1.1]FcRc (2.055(6) Å). The equivalent value for the Ru(IV) side is 2.220(25) Å, which is significantly longer than that for [1.1]FcRc (2.151(6) Å) and corresponds well to that for the Ru(IV) side in the [RcRcI]$^+$ cation (2.216(22) Å) [1]. Moreover, the distance between the Cp ring center and Ru(IV) is 1.861(8) Å, and the equivalent value on the Fe(II) side is 1.654(2) Å. Such expansion of the bond length may be due to the removal of bonding electrons (e_{2g}) on the Ru side.

The most interesting result in the structure analysis is the greatly twisted structure of C$_5$H$_4$CH$_2$C$_5$H$_4$ (C(6–10)–C(22)–C(16–20)) ligand, as shown in Fig. 2. The large dihedral angle (42.02°) is found between the Cp planes C(6)–C(10) and C(16)–C(20), (the small one (11.19°) is found between the planes C(1)–C(5) and C(11)–C(15)). In the case of the neutral [1.1]FcRc, the dihedral angle (18.6°) between the planes C(1)–C(5) and C(11)–C(15) corresponds well to that between the planes C(6)–C(10) and C(16)–C(20) (16.7°) [6]. Therefore, it may be expected that chemical shifts of C(16)–C(20) will be slightly different from those of C(11)–C(15) on the Ru(IV) side, as is shown by ^{13}C-CP/MAS NMR spectroscopy of **1**.

Fig. 3 shows ^{13}C-CP/MAS NMR spectra of [1.1]FcRc (a) and the single crystal salt **1** (b). Four sharp signals are observed for [1.1]FcRc. On the basis of the assignment of the ^{13}C-NMR spectroscopy of [1.1]FcRc in CDCl$_3$, the Cp-ring carbon atoms in the ferrocene and ruthenocene moieties appear at δ 69.27 and 71.98, respectively. The C$_1$ signals (δ 88.11) of the ferrocene and ruthenocene moieties are not well resolved. The –CH$_2$– signal is observed at δ 27.21. In contrast to the sharp signals observed for [1.1]FcRc,
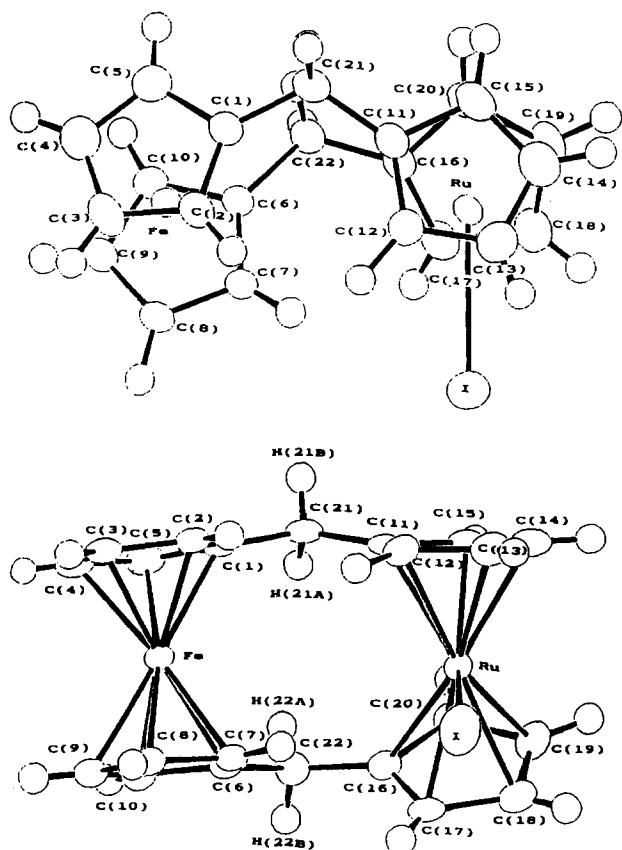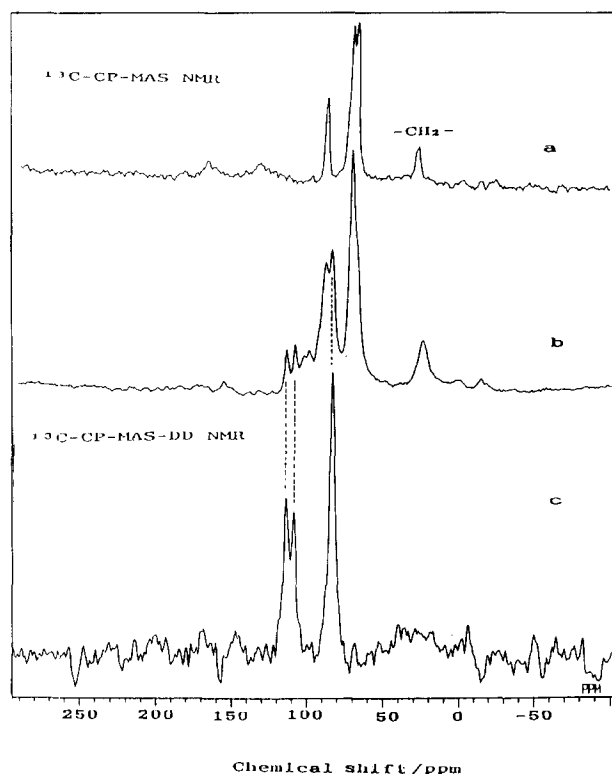
Fig. 3. ^{13}C CP/MAS NMR spectra of (a) [1.1]FcRc, (b) **1**, and (c) **1**, dipolar dephasing.

broader signals are found for **1**. A sharp signal at δ 70.92 is ascribed to the C atoms in the Cp ring the ferrocene moiety and three broader weak signals (δ 87.81, 99.08 and 102.85) are due to those in the ruthenocene moiety.

The reason for the broad signals on the Ru(IV) side must be the conformational difference in the planes C(11)–C(15) and C(16)–C(20). Moreover, it must be pointed out that under these conditions the relative peak intensities measured by the CP/MAS method are not a true measure of the abundances of the carbons, since not every carbon atom will have attained its optimum cross polarization and its optimum delay time. The peak intensity of C atoms in the ferrocene moiety corresponds well to that of the ruthenocene moiety by using without CP MAS NMR spectroscopy. Although a small lower-field shift (Δ δ) is observed for the ferrocene moiety (Δ $\delta = 1.65$), large shifts (Δ $\delta = 15.83$, 27.08 and 30.87) compared with the corresponding values on [1.1]FcRc are observed for the ruthenocene moiety. Similar shifts have already been reported for the [RcHI]$^+$I$_3^-$ salt in comparison with RcH [15]. The –CH$_2$– signal is observed at 24.49 ppm and the peak shows an upfield chemical shift (2.72 ppm) compared with the values for [1.1]FcRc, probably because of the conformational change.

The dipolar dephasing technique (DD) was applied to ascertain the assignment of C atoms. With increasing delay times for decoupling and data acquision, the signals ($\delta = 83.44$, 108.70 and 114.04) decayed slowly, supporting assignment to the C$_1$ signal (83.44 for the ferrocene moiety and 108.70 and 114.04 for the ruthenocene moiety), as shown in Fig. 3(c). The most interesting observation is the splitting of the C$_1$ signal (C(11), C(16)) for the ruthenocene moiety, which is due to the two different kinds of twisted C$_5$H$_4$CH$_2$C$_5$H$_4$ ligands, i.e. one has a large twisting angle and other has a small one, based on the results of X-ray structural analysis.
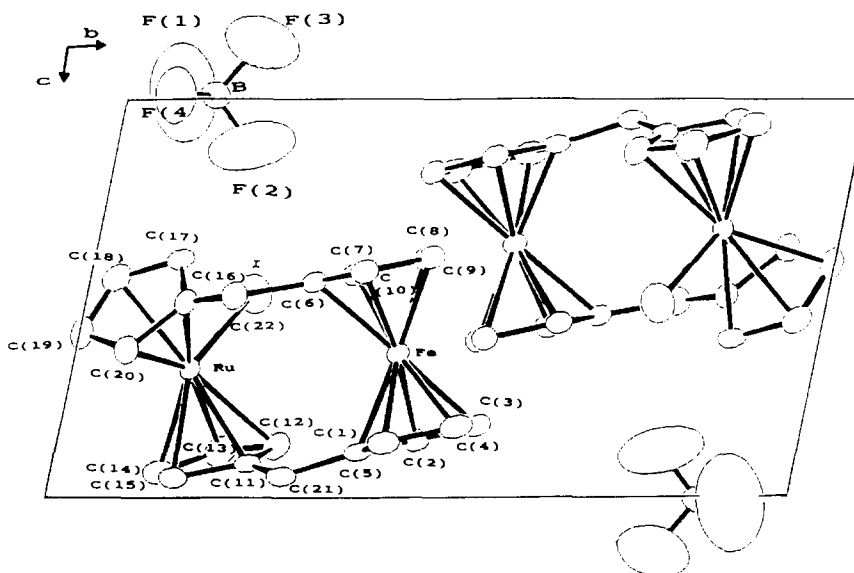

Fig. 4. Projection of the unit cell of **1** along the a axis.

A projection of the unit cell along the a axis is shown in Fig. 4. The tetrahedral BF_4^- shows greater thermal motion ($B_{eq} = 10.0$–25.6 Å^2) compared with that reported to the $[RcRcI]^+BF_4^-$ salt (7.0–9.5 Å^2). The average F–B–F angle is 109.4(34)° and the average B–F distance (1.26(8) Å) is slightly smaller than that in $[RcRcI]^+BF_4^-$ (1.36(2) Å), due to greater thermal motion. The shortest distance between F and I atoms is 3.737(12) Å (F(2)–I), this value is slightly longer than the sum of the van der Waals radii of I (2.15 Å) and F (1.35 Å). The shortest distances between each F atom and C atom in the Cp-ring are 3.462(19) Å for F(1)–C(20), 3.463(13) Å for F(2)–C(10), 3.177(12) Å for F(3)–C(14) and 3.051(19) Å for F(4)–C(14), i.e. the BF_4^- anion sits almost in van der Waals contact with the higher positive charge of the $[Cp(C_5H_4)Ru(IV)I]^+$ moiety. Therefore, the main reason for the difference between the twisting angles of the two $C_5H_4CH_2C_5H_4$ ligands may be electrostatic interaction between the $[Cp(C_5H_4)Ru(IV)I]^+$ moiety and the BF_4^- anion.

From the results obtained in the present study, it has been found that the oxidation product of [1.1]RcFc with iodoruthenocenium$^+BF_4^-$ is not a monocationic ferrocenium but a dicationic salt $[Fe(II)(C_5H_4CH_2C_5-H_4)_2)Ru(IV)I]^+$, owing to the greater stability of the Ru(IV)–I bond. The distance between Ru(IV) and Fe(II) (4.719 Å) is slightly shorter than that for neutral [1.1]FcRc (by about 0.07 Å), which leads to some interaction between them. Temperature-dependent [57]Fe-Mössbauer spectra were observed for salt 1. To obtain direct evidence of this interaction, detailed studies using techniques such as [57]Fe and [99]Ru Mössbauer spec-

troscopy should be carried out on 1 and related salts, e.g. $[1.1]FcRcI^+Y^-$ (Y = PF_6, I_3, picrate).

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