

## Molecular structure of chlororuthenocenium<sup>+</sup>BF<sub>4</sub><sup>-</sup> and chlorobiruthenocenium<sup>+</sup>BF<sub>4</sub><sup>-</sup> salts

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### Abstract

The structures of chlororuthenocenium<sup>+</sup>BF<sub>4</sub><sup>-</sup> ([RcHCl]<sup>+</sup>BF<sub>4</sub><sup>-</sup>, **1**) and chlorobiruthenocenium<sup>+</sup>BF<sub>4</sub><sup>-</sup> ([RcRcCl]<sup>+</sup>BF<sub>4</sub><sup>-</sup>, **2**) were determined by single-crystal X-ray diffraction studies. The crystal form of **1** is monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 7.801(6), *b* = 14.370(6), *c* = 10.422(3) Å, β = 91.91(4)°, *Z* = 4, with the final *R* = 0.032 and *R*<sub>w</sub> = 0.038. The cyclopentadienyl (Cp) rings in the cation are slanted greatly (dihedral angle, 34.54°) according to the Ru<sup>IV</sup>–Cl bond (2.417(2) Å) formation. The crystal form of **2** is monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 24.539(4), *b* = 10.627(5), *c* = 7.333(4) Å, β = 93.57(3)°, *Z* = 4, with the final *R* = 0.044 and *R*<sub>w</sub> = 0.033. The cation formulated as [Ru<sup>II</sup>Cp(C<sub>5</sub>H<sub>4</sub>C<sub>5</sub>H<sub>4</sub>)CpRu<sup>IV</sup>Cl]<sup>+</sup> exists in a trans-conformation, as in the case of neutral biruthenocene (RcRc). The distance between the Ru<sup>II</sup> and Ru<sup>IV</sup> (5.366(1) Å) indicates the absence of metal–metal interaction. The Cp and C<sub>5</sub>H<sub>4</sub> planes in the [Cp(C<sub>5</sub>H<sub>4</sub>)RuCl]<sup>+</sup> moiety are more slanted (dihedral angle, 39.98°) than that of **1**. Moreover, the fulvalene ligand (C<sub>5</sub>H<sub>4</sub>C<sub>5</sub>H<sub>4</sub>) is not planar owing to the repulsion between the Cl and the two C<sub>1</sub> atoms which connect the two C<sub>5</sub>H<sub>4</sub> moieties.

**Keywords:** Ruthenium; Metallocenes

### 1. Introduction

Intermolecular two-electron exchange reactions in the systems of ruthenocene–haloruthenocenium(IV) (RcH–RcHX<sup>+</sup>; X = Cl, Br, I) and osmocene–haloosmocenium(IV) (OcH–OcHX<sup>+</sup>) have been reported by Taube and co-workers [1] and Kirchner and co-workers [2–5]. All the studies suggest that the rate constants of the electron-exchange reactions increase in the order Cl < Br < I. We have reported some studies on electron-exchange reactions in mixed-valence halobiruthenocenium(II,IV)<sup>+</sup>Y<sup>-</sup> ([RcRcX]<sup>+</sup>Y<sup>-</sup>; X = Cl, Br, I; Y = BF<sub>4</sub>, PF<sub>6</sub>, I<sub>3</sub>), halodiethylbiruthenocenium(II,IV)<sup>+</sup>Y<sup>-</sup> ([RcRcEt<sub>2</sub>X]<sup>+</sup>Y<sup>-</sup>), halodipropylbiruthenocenium(II,IV)<sup>+</sup>Y<sup>-</sup> ([RcRcPr<sub>2</sub>X]<sup>+</sup>Y<sup>-</sup>) and haloethylbiruthenocenium(II,IV)<sup>+</sup>Y<sup>-</sup> ([RcRcEtX]<sup>+</sup>Y<sup>-</sup>) salts in acetone and other solvents by means of <sup>1</sup>H- and <sup>13</sup>C-

NMR spectroscopies [6–8]. One of the interesting features of the latter studies is the much greater rate constant of the reaction (XRu<sup>IV</sup>Ru<sup>II</sup> ⇌ Ru<sup>II</sup>Ru<sup>IV</sup>X) than that of the mononuclear mixed RcH–RcHX<sup>+</sup> and OcH–OcHX<sup>+</sup> systems. Although less temperature dependent <sup>1</sup>H-NMR spectra were observed for the RcH–RcHCl<sup>+</sup> system in acetone [9], remarkably temperature dependent <sup>1</sup>H-NMR spectra were observed for [RcRcCl]<sup>+</sup> even at lower temperatures (ca. 200 K). In addition, the rate constants order for the exchange reaction is the reverse of that in the mononuclear system, i.e. the rate increases in the order I < Br < Cl for binuclear systems; thus the order is not explained by the Ru–X bond strength alone.

Similar results were found for the [Ru<sup>II</sup>Cp(C<sub>5</sub>H<sub>4</sub>–CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)CpRu<sup>IV</sup>I]<sup>+</sup> cation obtained by the oxidation of diruthenocenyldimethane (RcCH<sub>2</sub>Rc) with I<sub>2</sub>. The same type of electron exchange reaction is observed, although the two ruthenocene moieties were connected by a non-conjugated –CH<sub>2</sub>– group. Hence, it was concluded that the electron exchange reaction takes place

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through the migration of X-atoms between the Ru<sup>II</sup> and Ru<sup>IV</sup> moieties [10].

Recently, the crystal structure of iodobiruthenocenium<sup>+</sup>BF<sub>4</sub><sup>-</sup> ([RcRcI]<sup>+</sup>BF<sub>4</sub><sup>-</sup>, **3**) salt was determined by X-ray analysis [11]. As in the case of neutral RcRc [12], the two Cp-rings are transoid with respect to the fulvalene ligand. The distance between the Ru<sup>II</sup> and Ru<sup>IV</sup> was found to be 5.467(1) Å, suggesting no interaction between them. Two interesting features are observed in **3**. The first is a large dihedral angle between the rings (42.4°) observed in the [Ru<sup>IV</sup>Cp(C<sub>5</sub>H<sub>4</sub>)]<sup>+</sup> moiety compared with that of the iodoruthenocenium cation ([RcHI]<sup>+</sup>, 32.2° [13]); the second is the non-planarity of the H<sub>4</sub>C<sub>5</sub>C<sub>5</sub>H<sub>4</sub> ligand due to the repulsion between the I and C<sub>1</sub> atoms. In the present paper the crystal structures of **1** and **2** are discussed in comparison with those of RcH, [RcHI]<sup>+</sup>, RcRc and **3**, which may provide a better understanding of the order of rate constants for the electron exchange reactions in the mononuclear RcH–RcHX<sup>+</sup> and binuclear [RcRcX]<sup>+</sup> systems.

## 2. Experimental

### 2.1. Syntheses

Salt **1** was prepared by a method similar to that used for [RcHCl]<sup>+</sup>PF<sub>6</sub><sup>-</sup> by using NaBF<sub>4</sub> in place of NH<sub>4</sub>PF<sub>6</sub>. Anal. Found: C, 33.95; H, 2.88. C<sub>10</sub>H<sub>10</sub>BClF<sub>4</sub>Ru. Calc.: C, 33.97; H, 2.85%. Salt **2** was prepared as follows: RcRc (100 mg, 0.22 mmol) dissolved in 50 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> was added to a stoichiometric amount of [RcHCl]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (101 mg, 0.227 mmol) dissolved in 200 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub>. The mixture was stirred for 1 h and the solvent was evaporated. After extraction of RcH with benzene, **2** was obtained by recrystallization from a CH<sub>2</sub>Cl<sub>2</sub>–C<sub>6</sub>H<sub>14</sub> mixture as deep purple crystals (90 mg; yield 70%). Anal. Found: C, 40.95; H, 3.18. C<sub>20</sub>H<sub>18</sub>BClF<sub>4</sub>Ru<sub>2</sub>. Calc.: C, 41.22; H, 3.11%. Single crystals of **1** and **2** suitable for X-ray studies were obtained by the method of hexane-vapor diffusion into CH<sub>2</sub>Cl<sub>2</sub> solutions.

### 2.2. Measurements

#### 2.2.1. X-ray crystallography

Crystals of **1** (0.4 × 0.4 × 0.3 mm<sup>3</sup>) and of **2** (0.1 × 0.2 × 0.3 mm<sup>3</sup>) were 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 (λ = 0.71073 Å). The intensity data were collected at 25 ± 1°C using the ω–2θ scan mode with a scanning speed of 4° min<sup>-1</sup>. The lattice parameters were determined by a least squares calculation with 25 reflections. Crystal stability

was checked by recording three standard reflections every 150 reflections, and no significant variations were observed. For **1**, 3751 reflections were collected in the range 4 ≤ 2θ ≤ 60°, 3523 were unique (R<sub>int</sub> = 0.011), of which 2935 reflections with I<sub>obsd</sub> > 2.0σ (I<sub>obsd</sub>) were used for the structure determination. The scan width was 1.21 + 0.3 tan θ. The refinement with 154 variable parameters converged to R = Σ||F<sub>o</sub>| – |F<sub>c</sub>|| / Σ|F<sub>o</sub>| = 0.032, R<sub>w</sub> = [Σw(|F<sub>o</sub>| – |F<sub>c</sub>||)<sup>2</sup> / ΣwF<sub>o</sub><sup>2</sup>]<sup>1/2</sup> = 0.038, where w = 4(Lp)<sup>2</sup>F<sub>o</sub><sup>2</sup> / [σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (pF<sub>o</sub><sup>2</sup>)<sup>2</sup>], Lp is the Lorentz-polarization factor, and p is the p-factor. The goodness of fit was 2.67. For **2**, 4986 reflections were collected in the range 4 ≤ 2θ ≤ 55°, 4636 were unique (R<sub>int</sub> = 0.031), of which 2652 reflections with I<sub>obsd</sub> > 1.5σ (I<sub>obsd</sub>) were used for the structure determination. The scan width was 0.73 + 0.3 tan θ. The refinement with 253 variable parameters converged to R = 0.044, R<sub>w</sub> = 0.033, and s = 1.84.

The non-hydrogen atoms were refined anisotropically by full matrix least squares. Hydrogen atoms were located based on difference Fourier maps, and were included isotropically in the refinement. Neutral atom scattering factors were taken from Cromer and Waber [14]; anomalous dispersion effect corrections were included [15], the values for Δf' and Δf'' were those of Creagh and McAuley [16]. All of the calculations were performed using the TEXSAN crystallographic software package [17]. Crystallographic data for **1** and **2** and some of the experimental conditions for the X-ray structure analysis are listed in Table 1.

Table 1  
Crystal and intensity collection data for **1** and **2**

	<b>1</b>	<b>2</b>
Formula	C <sub>10</sub> H <sub>10</sub> BClF <sub>4</sub> Ru	C <sub>20</sub> H <sub>18</sub> BClF <sub>4</sub> Ru <sub>2</sub>
Fw	353.52	582.76
Crystal dimensions (mm <sup>3</sup> )	0.4 × 0.4 × 0.3	0.1 × 0.2 × 0.3
Space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n
a (Å)	7.801(6)	24.539(4)
b (Å)	14.370(6)	10.627(5)
c (Å)	10.422(3)	7.333(4)
β (deg)	91.91(4)	93.57(3)
V (Å <sup>3</sup> )	1167(1)	1908(2)
Z	4	4
T (°C)	25	25
λ (Å)	0.71073	0.71073
μ (cm <sup>-1</sup> )	15.94	17.63
D <sub>x</sub> (g cm <sup>-3</sup> )	2.01	2.03
No. of reflections measured	3751	4986
No. of observed reflections	2935(I > 2σ(I))	2652(I > 1.5σ(I))
2θ scan range (deg)	4° ≤ 2θ ≤ 60°	4° ≤ 2θ ≤ 55°
Scan mode	ω–2θ	ω–2θ
Scan width	1.21 + 0.3 tan θ	0.73 + 0.3 tan θ
p	0.01	0.02
R	0.032	0.044
R <sub>w</sub>	0.038	0.033

### 3. Results and discussion

The final atomic coordinates and equivalent isotropic temperature factors of non-hydrogen atoms, selected bond distances and angles, and dihedral angles for **1** and **2** are shown in Tables 2–7 and ORTEP drawings of the cations **1** and **2** are shown in Figs. 1 and 2 respectively, along with the atom numbering system. As shown in Fig. 1, the Cl atom is coordinated to the Ru center. The Ru–Cl distance of **1** is 2.417(2) Å, which is 0.315 Å smaller than the value reported for Ru–I (2.732(3) Å) in [RcHI]<sup>+</sup> formulated as [Cp<sub>2</sub>Ru<sup>IV</sup>I]<sup>+</sup> cation [13] owing to the difference in the covalent radii of the I (1.33 Å) and Cl (0.99 Å) atoms.

The two Cp-rings keep good planarity (average least squares deviation of carbon atoms from the plane is 0.007 Å) and the rings remain eclipsed, as in the cases of neutral RcH and [RcHI]<sup>+</sup> cation. The average C–C distance (1.41(4) Å) is comparable with that of RcH (1.43 ± 0.03 Å). The average distances from Ru to Cp-rings and C atoms are 1.864(1) Å and 2.218(11) Å respectively, which are comparable with those for [Cp<sub>2</sub>Ru<sup>IV</sup>I]<sup>+</sup> cation (1.84 × 0.012 Å and 2.197 ± 0.012 Å respectively [13]); therefore, it can be concluded that the formal oxidation state of the Ru is Ru<sup>IV</sup> and the cation is formulated as [ClRu<sup>IV</sup>Cp<sub>2</sub>]<sup>+</sup>. The conclusion is comparable with the results of the <sup>1</sup>H- and <sup>13</sup>C-CP–MAS NMR spectroscopies of **1** [9,18].

The distances from Cl to C(1), C(5), C(6) and C(10) are 3.019(6), 3.038(6) Å, 2.984(5) Å and 2.978(5) Å respectively; these are much smaller than the values of other Cl ··· C distances (cf. Cl ··· C(3), 4.343(5) Å), and are less than the sum of the van der Waals radii

Table 2  
Atomic coordinates (×10<sup>4</sup>) and isotropic temperature factors for **1** (Å<sup>2</sup> × 10<sup>2</sup>)

Atom	x	y	z	B <sub>eq</sub> <sup>a</sup>
Ru	3648.0(4)	4465.7(2)	7387.4(3)	2.7
Cl	5956(2)	5589(1)	7454(1)	5.3
C(1)	2112(8)	5750(3)	7086(6)	5.6
C(2)	1062(6)	5102(4)	7598(5)	4.8
C(3)	942(6)	4340(4)	6747(5)	4.7
C(4)	1914(7)	4538(4)	5653(5)	5.2
C(5)	2667(8)	5390(5)	5832(5)	5.9
C(6)	5280(6)	3870(3)	8964(4)	4.1
C(7)	3635(6)	3538(3)	9095(4)	4.3
C(8)	3162(6)	3022(3)	7976(5)	4.3
C(9)	4589(7)	3014(3)	7148(5)	4.5
C(10)	5880(5)	3526(3)	7726(5)	4.4
B	9322(7)	2849(4)	10018(5)	4.2
F(1)	9198(5)	3753(3)	9655(4)	8.5
F(2)	7827(5)	2543(3)	10508(4)	7.7
F(3)	9707(7)	2349(4)	9006(5)	13.3
F(4)	10609(5)	2820(4)	10916(4)	10.0

<sup>a</sup> B<sub>eq</sub> = 4/3(B<sub>11</sub>a<sup>2</sup> + B<sub>22</sub>b<sup>2</sup> + B<sub>33</sub>c<sup>2</sup> + B<sub>13</sub>ac cos β); B<sub>ij</sub> is defined as exp[-(h<sup>2</sup>B<sub>11</sub> + k<sup>2</sup>B<sub>22</sub> + l<sup>2</sup>B<sub>33</sub> + 2klB<sub>23</sub> + 2hlB<sub>13</sub> + 2hkB<sub>12</sub>)].

Table 3

Atomic coordinates (×10<sup>4</sup>) and isotropic temperature factors for **2** (Å<sup>2</sup> × 10<sup>2</sup>)

Atom	x	y	z	B <sub>eq</sub> <sup>a</sup>
Ru(1)	1866.9(3)	5678.1(5)	1373.4(9)	2.3
Ru(2)	319.9(3)	2515.7(7)	-1364.2(9)	2.2
Cl	1544(1)	4516(2)	3897(3)	3.7
C(1)	2750(4)	6149(9)	1841(8)	4.4
C(2)	2517(4)	6130(4)	3472(9)	4.5
C(3)	2104(4)	7070(9)	3460(10)	4.7
C(4)	2088(4)	7673(9)	1781(2)	4.9
C(5)	2479(4)	7086(10)	742(6)	4.8
C(6)	1180(3)	4206(8)	25(9)	2.3
C(7)	1052(3)	5527(8)	-151(8)	2.7
C(8)	1441(4)	6103(9)	-1243(6)	3.2
C(9)	1847(3)	5178(9)	-1499(10)	3.0
C(10)	1719(3)	4055(8)	-602(5)	2.7
C(11)	855(3)	3253(8)	826(10)	2.2
C(12)	290(3)	3424(8)	1262(9)	2.7
C(13)	63(3)	2194(9)	1432(6)	3.3
C(14)	463(4)	1297(9)	1062(9)	3.2
C(15)	952(4)	1930(9)	652(8)	3.0
C(16)	-281(4)	1906(9)	-3472(5)	4.2
C(17)	-225(4)	3215(9)	-3632(2)	3.7
C(18)	314(4)	3494(9)	-3961(9)	3.1
C(19)	587(8)	2321(4)	-4120(10)	4.1
C(20)	220(4)	1353(9)	-3780(9)	4.9
B	1614(5)	-472(8)	7210(9)	3.8
F(1)	1821(2)	718(6)	7527(8)	5.5
F(2)	2036(2)	-1319(6)	7273(9)	5.8
F(3)	1274(3)	-757(9)	8569(9)	7.8
F(4)	1349(2)	-498(7)	5575(9)	8.1

<sup>a</sup> B<sub>eq</sub> = 4/3(B<sub>11</sub>a<sup>2</sup> + B<sub>22</sub>b<sup>2</sup> + B<sub>33</sub>c<sup>2</sup> + B<sub>13</sub>ac cos β); B<sub>ij</sub> is defined as exp[-(h<sup>2</sup>B<sub>11</sub> + k<sup>2</sup>B<sub>22</sub> + l<sup>2</sup>B<sub>33</sub> + 2klB<sub>23</sub> + 2hlB<sub>13</sub> + 2hkB<sub>12</sub>)].

(3.50 Å) of C and Cl atoms [19]. Avoiding steric hindrance between them, the two Cp-rings are slanted greatly, as shown in Fig. 1. The shortest and largest C ··· C distances between the two planes are 2.84(1) (C(3) ··· C(8)) and 4.12(1) Å (C(5) ··· C(10)) respectively. The dihedral angle between them is 34.54°, which is significantly larger than the value of [RcHI]<sup>+</sup> cation (32.2° [13]) owing to the much shorter Ru–Cl bond distance. This difference seems to be related to the

Table 4  
Interatomic distances (Å) for **1**

Ru–Cl	2.417(2)	Ru–C(1)	2.217(5)
Ru–C(2)	2.233(4)	Ru–C(3)	2.200(5)
Ru–C(4)	2.224(5)	Ru–C(5)	2.212(5)
Ru–C(6)	2.217(4)	Ru–C(7)	2.225(4)
Ru–C(8)	2.199(4)	Ru–C(9)	2.229(4)
Ru–C(10)	2.222(4)	C(1)–C(2)	1.36(1)
C(2)–C(3)	1.41(1)	C(3)–C(4)	1.42(1)
C(4)–C(5)	1.37(1)	C(5)–C(1)	1.48(1)
C(6)–C(7)	1.38(1)	C(7)–C(8)	1.42(1)
C(8)–C(9)	1.43(1)	C(9)–C(10)	1.37(1)
C(10)–C(6)	1.47(1)	B–F(1)	1.36(1)
B–F(2)	1.36(1)	B–F(3)	1.32(1)
B–F(4)	1.35(1)		

Table 5  
Interatomic distances (Å) for **2**

Ru(1)–Cl	2.400(2)	Ru(2)–Cl	5.195(2)
Ru(1)–Ru(2)	5.366(1)	Ru(1)–C(1)	2.231(9)
Ru(1)–C(2)	2.201(9)	Ru(1)–C(3)	2.182(10)
Ru(1)–C(4)	2.204(10)	Ru(1)–C(5)	2.190(9)
Ru(1)–C(6)	2.462(8)	Ru(1)–C(7)	2.235(8)
Ru(1)–C(8)	2.172(8)	Ru(1)–C(9)	2.170(8)
Ru(1)–C(10)	2.265(8)	Ru(2)–C(11)	2.157(8)
Ru(2)–C(12)	2.159(8)	Ru(2)–C(13)	2.211(8)
Ru(2)–C(14)	2.212(8)	Ru(2)–C(15)	2.168(9)
Ru(2)–C(16)	2.170(10)	Ru(2)–C(17)	2.198(9)
Ru(2)–C(18)	2.166(8)	Ru(2)–C(19)	2.171(9)
Ru(2)–C(20)	2.161(6)	C(1)–C(2)	1.36(1)
C(2)–C(3)	1.42(1)	C(3)–C(4)	1.39(1)
C(4)–C(5)	1.41(1)	C(5)–C(1)	1.42(1)
C(6)–C(7)	1.44(1)	C(7)–C(8)	1.42(1)
C(8)–C(9)	1.42(1)	C(9)–C(10)	1.41(1)
C(10)–C(6)	1.44(1)	C(11)–C(12)	1.45(1)
C(12)–C(13)	1.43(1)	C(13)–C(14)	1.41(1)
C(14)–C(15)	1.43(1)	C(15)–C(11)	1.43(1)
C(16)–C(17)	1.40(1)	C(17)–C(18)	1.39(1)
C(18)–C(19)	1.43(1)	C(19)–C(20)	1.40(1)
C(20)–C(16)	1.39(1)	B–F(1)	1.38(1)
B–F(2)	1.37(1)	B–F(3)	1.37(1)
B–F(4)	1.33(1)		

value of activation energy  $E_a$  for the intermolecular electron exchange reaction in  $\text{RcH-RcHX}^+$  systems, as indicated in  $\text{Ru}^{\text{II}}\text{Cp}_2 + \text{XRu}^{\text{IV}}\text{Cp}_2^+ \rightleftharpoons \text{XRu}^{\text{II}}\text{Cp}_2^+ + \text{Ru}^{\text{IV}}\text{Cp}_2$ . As reported in the previous  $^1\text{H-NMR}$  spectroscopic studies of  $\text{RcH-RcHX}^+$  (1:1 molar ratio) systems in acetone, temperature-dependent NMR spectra (183–293 K) were observed for  $\text{RcH-RcHI}^+$  and

Table 7  
Dihedral angles (deg) between planes for **2**

Plane	Plane		
	C(6)–C(10)	C(11)–C(15)	C(16)–C(20)
C(1)–C(5)	39.98	60.91	59.88
C(6)–C(10)	—	21.00	20.01
C(11)–C(15)	—	—	4.36

$\text{RcH-RcHBr}^+$  systems [9]. The  $E_a$  values are calculated to be  $30.6 \text{ kJ mol}^{-1}$  and  $41.7 \text{ kJ mol}^{-1}$  respectively. In contrast, less temperature dependence (183–373 K) was observed for the  $\text{RcH-RcHCl}^+$  system because of its higher  $E_a$  value ( $47.9 \text{ kJ mol}^{-1}$ ). Two of the most important reasons for the higher  $E_a$  value for  $\text{RcH-RcHCl}^+$ , compared with those of  $\text{RcH-RcHI}^+$  and  $\text{RcH-RcHBr}^+$  systems, are the Ru–X bond strength (the strength increases in the order  $\text{I} < \text{Br} < \text{Cl}$ , as reported by Kirchner et al. [3]) and the large configurational change including the dihedral angle from  $\text{RcH}$  to the  $[\text{RcHX}]^+$ . As both values for  $\text{RcH-RcHCl}^+$  system are larger than the corresponding values for the other systems, the higher  $E_a$  value for  $\text{RcH-RcHCl}^+$  is obtained, provided that the structure of the cations in a solid remain intact in organic solutions.

Figs. 2 and 3 show an ORTEP drawing of the cationic moiety of **2**. As has been reported for neutral  $\text{RcRc}$  and cation of **3** [18], the cation exists in a transoid structure. As in the case of **1**, Cl atom is coordinated to Ru(1) with the Ru(1)–Cl distance of  $2.400(2) \text{ \AA}$ , which is slightly smaller than the value for the  $\text{Ru}^{\text{IV}}\text{-Cl}$  in **1**

Table 6  
Bond angles (deg) for **1** and **2**

<b>1</b>			
C(1)–C(2)–C(3)	108.2(5)	C(2)–C(3)–C(4)	108.9(5)
C(3)–C(4)–C(5)	107.9(5)	C(4)–C(5)–C(1)	107.2(5)
C(5)–C(1)–C(2)	107.7(5)	C(6)–C(7)–C(8)	108.4(4)
C(7)–C(8)–C(9)	108.3(4)	C(8)–C(9)–C(10)	107.7(4)
C(9)–C(10)–C(6)	108.4(4)	C(7)–C(6)–C(10)	107.1(4)
F(1)–B–F(2)	111.1(5)	F(1)–B–F(3)	108.4(5)
F(1)–B–F(4)	105.5(5)	F(2)–B–F(3)	110.1(5)
F(2)–B–F(4)	110.9(5)	F(3)–B–F(4)	110.8(6)
<b>2</b>			
C(1)–C(2)–C(3)	108.0(10)	C(2)–C(3)–C(4)	108.1(10)
C(3)–C(4)–C(5)	107.3(10)	C(4)–C(5)–C(1)	108.0(9)
C(5)–C(1)–C(2)	107.0(10)	C(6)–C(7)–C(8)	108.5(8)
C(7)–C(8)–C(9)	106.2(8)	C(8)–C(9)–C(10)	110.2(7)
C(9)–C(10)–C(6)	106.9(8)	C(6)–C(11)–C(12)	124.3(8)
C(11)–C(12)–C(13)	106.7(8)	C(12)–C(13)–C(14)	108.8(7)
C(13)–C(14)–C(15)	109.1(8)	C(14)–C(15)–C(11)	107.3(8)
C(20)–C(16)–C(17)	108.0(10)	C(16)–C(17)–C(18)	108.9(9)
C(17)–C(18)–C(19)	106.5(9)	C(18)–C(19)–C(20)	108.5(8)
C(19)–C(20)–C(16)	107.7(10)	F(1)–B–F(2)	109.0(9)
F(1)–B–F(3)	108.1(9)	F(1)–B–F(4)	119.0(10)
F(2)–B–F(3)	108.8(10)	F(2)–B–F(4)	110.2(10)
F(3)–B–F(4)	111.0(10)		

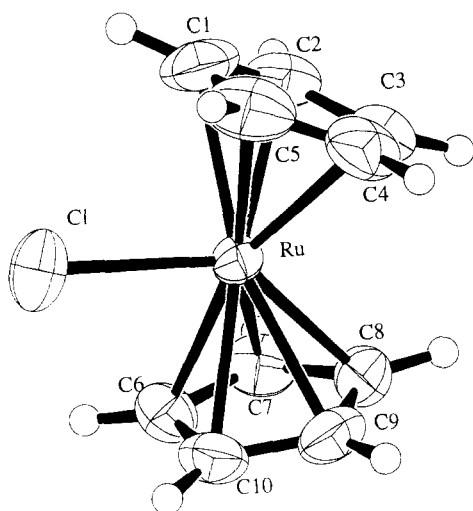


Fig. 1. ORTEP drawing of the cation of **1** with the numbering scheme of the atoms.

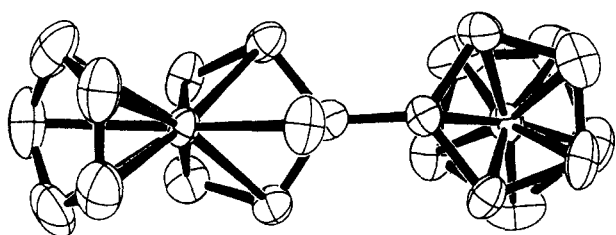


Fig. 2. ORTEP drawing of the cation of **2** with the numbering scheme of the atoms.

(2.417(2) Å). The Ru(2)···Cl and Ru(2)···Ru(1) distances are 5.195(2) Å and 5.366(1) Å respectively, suggesting no interaction between them, although the latter distance is smaller than the corresponding value of **3** (5.464(4) Å). Oxidation states of Ru(1) and Ru(2) are assigned to Ru<sup>IV</sup> and Ru<sup>II</sup> respectively, and the cation is formulated as [ClRu<sup>IV</sup>Cp(C<sub>5</sub>H<sub>4</sub>C<sub>5</sub>H<sub>4</sub>)CpRu<sup>II</sup>]<sup>+</sup>. The mean distances from Ru<sup>IV</sup> and Ru<sup>II</sup> to the rings are 1.873(3) Å and 1.813(4) Å respectively, corresponding well to those of **3** (1.879(7) Å and 1.812(3) Å respectively).

The dihedral angles between the Cp and C<sub>5</sub>H<sub>4</sub> ligands of Ru<sup>IV</sup> and Ru<sup>II</sup> are 39.98 and 4.36° respectively. The former value is much larger than the value for the cation **1** (34.54°). Although the two rings in the Ru<sup>II</sup> moiety are nearly eclipsed, as in the case of **1** and R<sub>c</sub>H, the rings in the Ru<sup>IV</sup> moiety are nearly staggered, as

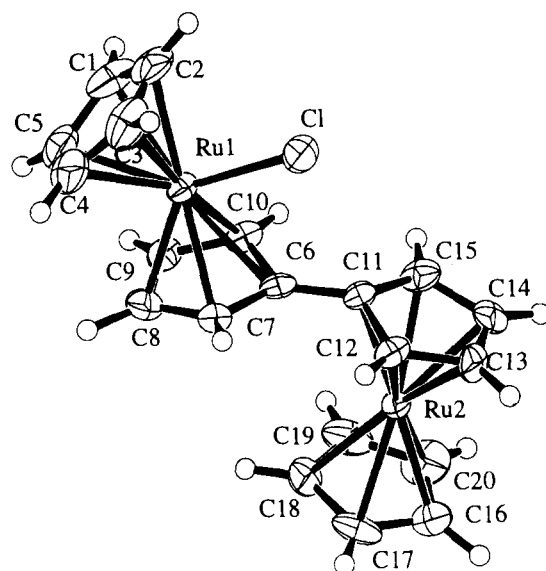


Fig. 3. ORTEP drawing of the conjugated fulvalene ligand of **2** with the numbering scheme of the atoms.

shown in Fig. 2. The distances between C(5)···C(9) (2.98(1) Å) and C(4)···C(8) (3.13(1) Å) are much smaller than the values of C(3)···C(7) (3.94(1) Å) and C(2)···C(6) (4.51(1) Å) and are smaller than the sum of the van der Waals radii of two C atoms (3.40 Å); i.e. the Cp-rings in the Ru<sup>IV</sup> moiety may sit in a staggered conformation in order to reduce the interannular steric hindrance between them.

The most interesting features for the cation **2** are the non-planarity of the C<sub>5</sub>H<sub>4</sub> ligand (C(6–10)) of the Ru<sup>IV</sup> side and the fulvalene system (H<sub>4</sub>C<sub>5</sub>C<sub>5</sub>H<sub>4</sub>), shown in Scheme 1. The average least squares deviation of the C atoms (C(6–10)) from the plane is 0.054 Å, which is much larger than the corresponding values of other planes (0.009 Å; C(1–5) and 0.012 Å; C(11–15)). The dihedral angle between the plane (C(6)–C(7)–C(10)) and the plane C(7–10) is 13.41°. Moreover, the dihedral angle between the planes C(6–10) and C(11–15) is 20.01°. The distances of Cl···C(6) and Cl···C(11) are 2.942 Å and 3.044(8) Å respectively, which are less than the sum of the van der Waals radii (3.50 Å) of Cl and C atoms. Owing to the steric hindrance between the Cl and C(6) atoms, the C(6) atom is located largely out of the plane (0.072 Å), resulting in a much longer Ru(1)–C(6) bond length (2.462(8) Å) compared with

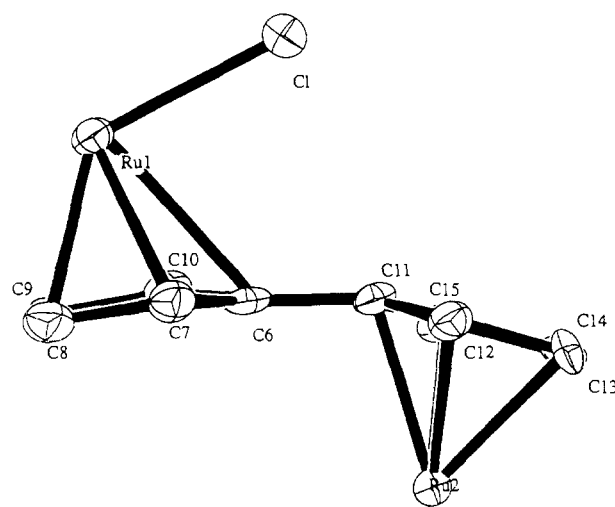
Table 8  
Relation between  $E_a$ , dihedral angle and Ru<sup>IV</sup>–X values for **1–3** and related salt [R<sub>c</sub>HI]<sup>+</sup>

Compound	$E_a$ (kJ mol <sup>-1</sup> )	Dihedral angle (deg)	Ru <sup>IV</sup> –X distance (Å)
<b>1</b>	47.9	34.54 <sup>a</sup>	2.417(2) (X = Cl)
[R <sub>c</sub> HI] <sup>+</sup>	30.6	32.2 <sup>a</sup>	2.732(3) <sup>c</sup> (X = I)
<b>2</b>	32.8	39.98 <sup>a</sup> 13.41 <sup>b</sup>	2.400(2) (X = Cl)
<b>3</b>	36.5	42.4 <sup>a</sup> 19.35 <sup>b</sup>	2.717(2) <sup>d</sup> (X = I)

<sup>a</sup> Between the two cyclopentadienyl rings of the Ru<sup>IV</sup> side. <sup>b</sup> Between the C(6)–C(7)–C(10) and the C(7–10) planes. <sup>c</sup> Ref. [13]. <sup>d</sup> Ref. [11].

those of other Ru(1)–C distances (2.170–2.265 Å). The larger dihedral angle (39.98°) between the Cp and C<sub>5</sub>H<sub>4</sub> planes, compared with the corresponding value (34.54°) in the mononuclear **1** cation and the non-planarity of the C<sub>5</sub>H<sub>4</sub> ligand (C(6–10)) in the Ru<sup>IV</sup> moiety of **2**, is explained by the same reason. These structural features increase for the cation **3**; i.e. a much larger dihedral angle of the C(6)–C(7)–C(10) and C(7–10) (19.35°) and a larger dihedral angle of the Cp and C<sub>5</sub>H<sub>4</sub> planes (42.4°) are observed for the cation **3** compared with those of the cation **2** (13.41° and 39.98° respectively), probably because of large van der Waals radius of I.

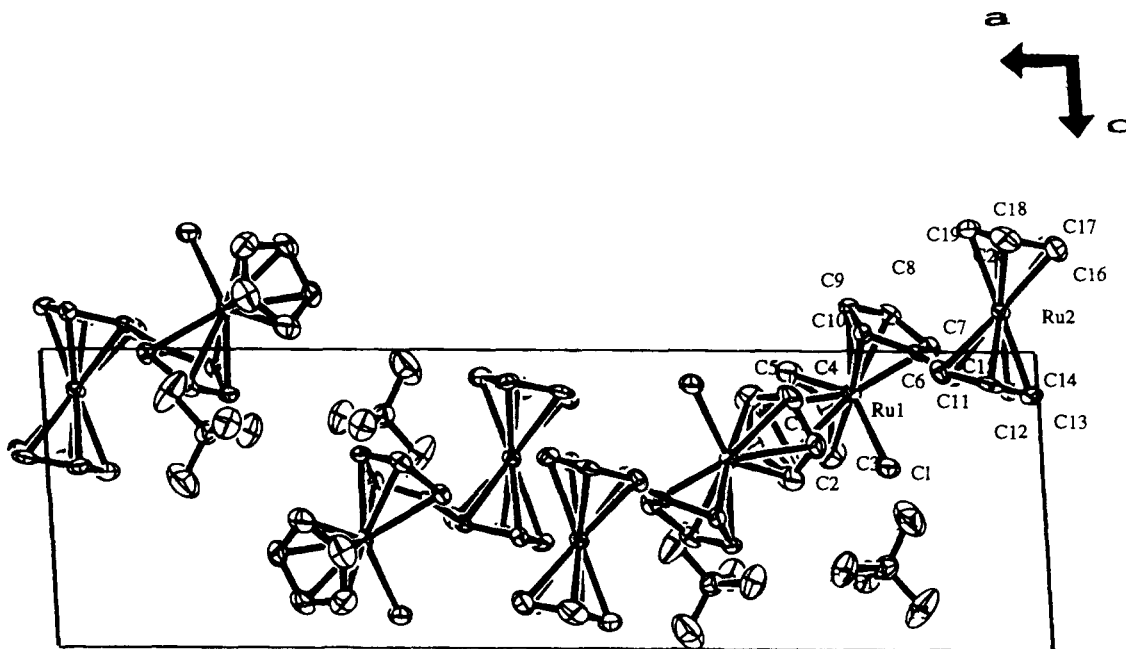
As already mentioned in the Introduction, an electron exchange reaction occurs between the Ru<sup>II</sup> and Ru<sup>IV</sup> atoms with X<sup>−</sup> migration in the binuclear [RcRcX]<sup>+</sup>, [RcRcEt<sub>2</sub>X]<sup>+</sup> and [RcRcPr<sub>2</sub>X]<sup>+</sup> (X = Cl, Br, I) [RcRcX]<sup>+</sup> systems in solution, expressed as [XRu<sup>IV</sup>Cp(C<sub>5</sub>H<sub>4</sub>–C<sub>5</sub>H<sub>4</sub>)CpRu<sup>II</sup>]<sup>+</sup> ⇌ [Ru<sup>II</sup>Cp(C<sub>5</sub>H<sub>4</sub>C<sub>5</sub>H<sub>4</sub>)CpRu<sup>IV</sup>I]<sup>+</sup> [6–8]. All the results reported previously indicate that the rate increases in the order Cl > Br > I; i.e. the *E*<sub>a</sub> values of the reaction decrease in the order (36.5 kJ mol<sup>−1</sup>, 34.0 kJ mol<sup>−1</sup> and 32.8 kJ mol<sup>−1</sup> for [RcRcI]<sup>+</sup>, [RcRcBr]<sup>+</sup> and [RcRcCl]<sup>+</sup> respectively [8]). Based on the results of X-ray diffraction studies on **3** and **2**, it has been found that the non-planarity of the C<sub>5</sub>H<sub>4</sub> ligand (C(6–10)) and the dihedral angle between the Cp and C<sub>5</sub>H<sub>4</sub> planes on the Ru<sup>IV</sup> moiety are related strongly to the *E*<sub>a</sub> values; i.e. both the values for **2** are smaller than the corresponding values for **3**, see Table 8. The most important reason for the lower *E*<sub>a</sub> value of the **2** cation compared with that of the **3** cation may be



Scheme 1.

due to the smaller configurational change from the Rch moiety to the haloruthenocenium cation.

A projection of the unit cell along the *b* axis is shown in Fig. 4. The shortest intermolecular Ru ⋯ Ru and C ⋯ C distances are 5.699(1) Å and 3.67(1) Å (C(1) ⋯ C(15)) respectively, showing no intermolecular interaction between the cations. The mean B–F distance and F–B–F angle are found to be 1.36(1) Å and 109.5(13)° respectively. These values are similar to those for **1** (1.35(2) Å, 108(3)°) and **3** (1.364(16) Å and 109.5(18)°). The shortest distances between each F atom and C atom in the Cp-ring are 3.29(1) Å for F(1) ⋯ C(2), 3.19(1) Å for F(2) ⋯ C(5), 3.36(1) Å

Fig. 4. Projection of the unit cell of **2** along the *b* axis.

for F(3) ··· C(15) and 3.40(1) Å for F(4) ··· C(1). The shortest distance is slightly larger than the sum of the van der Waals radii (3.05 Å) of C and F. Moreover, the distances between the F(2) ··· H(8) (2.463 Å) and F(3) ··· H(8) (2.236 Å) (which are much closer the sum of van der Waals radii (2.55 Å) of F and H) indicate the presence of hydrogen bonds between them, resulting in the smaller thermal motion ( $B_{\text{eq}} = 5.5\text{--}8.1$ ) of  $\text{BF}_4^-$  compared with the value for **1** and the stabilization of the higher positive  $[\text{Cp}(\text{C}_5\text{H}_4)\text{Ru}^{\text{IV}}\text{Cl}]^+$  moiety in the solid.

On the basis of the present studies, it may be concluded that the reason why the  $E_a$  order of the X-atom exchange reactions in mononuclear  $\text{RcH-RcHX}^+$  systems is the reverse of that in the binuclear systems can be explained without contradiction by the structural point of view; i.e. the large configurational change from the Rc moiety to the haloruthenocenium moiety gives a higher  $E_a$  value.

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