

as  $\sim 1.44$  V. Marcus cross-correlations from the present data then predict a self-exchange rate of  $\sim 50 \text{ M}^{-1}\text{s}^{-1}$  for the hydroxo couple. Few other data are available where the outer-sphere pathway of  $\text{CoOH}^{2+}$  may be assigned. In the reaction with the Ni(II) oxime ligand complex ( $L = 3,14$ -dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime) where the  $\text{NiN}_6$  configuration is maintained on oxidation,<sup>33</sup> the calculated self-exchange rate for  $\text{CoOH}^{2+/+}$  is  $\sim 2 \text{ M}^{-1}\text{s}^{-1}$ , which compares reasonably with that from the present study. More data on the spin states of the  $\text{CoOH}^{2+}$  ion are required before substantive discussion may be made of these results. It is of interest, however, that from the value of  $k(\text{CoOH}^{2+/+}) = 50 \text{ M}^{-1}\text{s}^{-1}$ , the predicted rate for the reaction of  $\text{CoOH}^{2+}$  with  $\text{Ni}^{\text{II}}(\text{cyclam})^{2+}$  is  $4.1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ , compared with an observed rate constant of  $4.4 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ . The reaction may thus involve an outer-sphere pathway. The corresponding calculation for the  $\text{Ni}[\text{Me}_6[14]-4,11\text{-diene}]^{2+}$  complex predicts a value of  $\sim 1.1 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$ , about 4 orders of magnitude lower than that observed ( $2.55 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ ). We are currently attempting to prepare other Ni(II/III) couples involving  $\text{NiN}_6$  chromophores that will provide further details on these reactions.

Although this discussion has centered round the possible self-exchange rate of the  $\text{CoOH}^{2+/+}$  couple, the origin of the pH dependence could derive from an intramolecular  $\text{NiL}_2\text{-Co}$  hydrogen-bonding interaction or from a proton transfer coupled to the electron-transfer step. Davies<sup>35</sup> has analyzed the var-

iations in rate constants for outer-sphere reactions of  $\text{CoOH}^{2+}$  in terms of outer-sphere precursor formation and the attainment of a species in which the distribution of  $\text{OH}^-$  in the inner sphere of the cobalt(III) is optimal for hydroxide-mediated electron transfer within the precursor complex. Specific interactions between the H atoms of the secondary amine and the  $\text{CoOH}^{2+}$  cannot be ruled out at this stage.

The preparation of a very stable  $\text{Ni}^{\text{III}}\text{N}_6^{2+/3+}$  couple has enabled us to gain further insights into the redox behavior of these  $d^7/d^8$  systems and in addition has provided support for the outer-sphere character of reactions of aquacobalt(III). Details of the crystal structure of the  $\text{Ni}^{\text{III}}(\text{nonaneN}_3)_2^{3+}$  ion will enable us to identify intrinsic contributions to the activation energy attributable to first-coordination-sphere reorganization. Such effects are considered to be much smaller for Ni than for similar systems involving other metal ions (e.g. Co) and may account for the generally higher self-exchange rates.

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**Registry No.** L-3HCl, 58966-93-1; L-Ts<sub>3</sub>, 52667-89-7;  $\text{Co}^{3+}(\text{aq})$ , 15275-05-5;  $\text{CoOH}^{2+}$ , 68842-90-0;  $\text{Co}(\text{phen})_3(\text{ClO}_4)_2$ , 15317-76-7;  $\text{NiL}_2(\text{ClO}_4)_2$ , 60296-44-8;  $\text{NiL}_2(\text{ClO}_4)_3$ , 86709-82-2;  $\text{I}^-$ , 20461-54-5;  $\text{NOPF}_6$ , 16921-91-8;  $N,N',N''$ -tritosyldiethylenetriamine, disodium salt, 52601-80-6; 1,2-ethanediol ditosylate, 6315-52-2;  $N,N',N''$ -tritosyldiethylenetriamine, 56187-04-3.

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## Reactivity of Haloruthenocene(IV) Complexes

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The ruthenium(IV)-containing compounds  $[\text{Ru}(\text{cp})_2\text{Br}]\text{PF}_6$  and  $[\text{Ru}(\text{cp})_2\text{Cl}]\text{PF}_6$  react with  $\text{H}_2\text{O}$ , yielding ruthenocene and ring-oxidation products,  $\text{Ru}(\text{cp})(\text{cpO})\text{Br}$  and  $\text{Ru}(\text{cp})(\text{cpO})\text{Cl}$ , respectively. The structure of the oxidized bromo compound has been determined from 564 unique x-ray reflections. The compound crystallizes in the orthorhombic space group  $Pnma$  with unit cell dimensions  $a = 13.588$  (2) Å,  $b = 8.876$  (1) Å,  $c = 7.495$  (1) Å,  $V = 904$  (1) Å<sup>3</sup>, and  $Z = 4$ . The discrepancy indices are  $R_1 = 3.05\%$  and  $R_2 = 3.51\%$ . A mirror plane, containing the ruthenium and bromine atoms, bisects the cyclopentadienyl and cyclopentadienone (cpO) rings. The rings are in a staggered conformation and are bent away from the halide.

### Introduction

The chemical and electrochemical oxidations of the iron-group metallocenes have been extensively examined.<sup>3-10</sup> When ferrocene or osmacene is oxidized electrochemically, a one-electron change is observed. Surprisingly, when ruthenocene is electrochemically oxidized, a two-electron change is realized. Whereas ferrocene is oxidized to the ferrocenium cation by

the halogens, both osmacene and ruthenocene form complexes of the general form  $\text{M}(\text{cp})_2\text{X}^+$  in which the metal is in the oxidation state 4+ and can be considered to be seven-coordinated. Gray et al.<sup>3</sup> have determined the structure of the triiodide salt of  $\text{Ru}(\text{cp})_2\text{I}^+$  by X-ray diffraction methods. The chemistry of these high-oxidation-state organometallic complexes has not been previously explored. In this paper we report the reaction of the Ru(IV) complexes with  $\text{H}_2\text{O}$  and the structure of one of the products of this kind of reaction.

### Experimental Section

**Materials.** Ruthenocene was purchased from Strem Chemical, Inc.  $[\text{Ru}(\text{cp})_2\text{X}]\text{X}_3$ . The compounds with  $\text{X} = \text{Br}$  or  $\text{I}$  were prepared as described in the literature.<sup>5</sup> That with  $\text{X} = \text{Cl}$  has not heretofore been prepared, but it is readily formed following the procedure used for the other two complexes. Anal. Calcd for  $\text{C}_{10}\text{H}_{10}\text{RuCl}_4$ : C, 32.19; H, 2.70; Cl, 38.01; Ru, 27.09. Found: C, 31.68; H, 2.47; Cl, 37.02; Ru, 26.80. Satisfactory carbon, hydrogen, and halogen analyses were obtained for all other new compounds.

$[\text{Ru}(\text{cp})_2\text{Cl}]\text{PF}_6$ . A 0.50-g sample of  $\text{Ru}(\text{cp})_2$  was dissolved in 50 mL of benzene and the resultant mixture added to 25 mL of 4 M

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Table I. Crystallographic Data

formula	RuC <sub>10</sub> H <sub>9</sub> OBr
space group	<i>Pnma</i>
<i>a</i> , Å	13.588 (2)
<i>b</i> , Å	8.876 (1)
<i>c</i> , Å	7.495 (1)
<i>V</i> , Å <sup>3</sup>	904 (1)
<i>Z</i>	4
cryst size, mm	0.15 × 0.15 × 0.15
$\mu$ , cm <sup>-1</sup>	43.9
range of 2 $\theta$ , deg	3–45
no. of unique data	637
data with $F_o^2 > 3\sigma(F_o^2)$	564
<i>R</i> <sub>1</sub>	0.0305
<i>R</i> <sub>2</sub>	0.0351
color of cryst	red-brown
habit of cryst	bladed
temp of data collen	ambient
octant colled	+ <i>h</i> , + <i>k</i> , + <i>l</i>

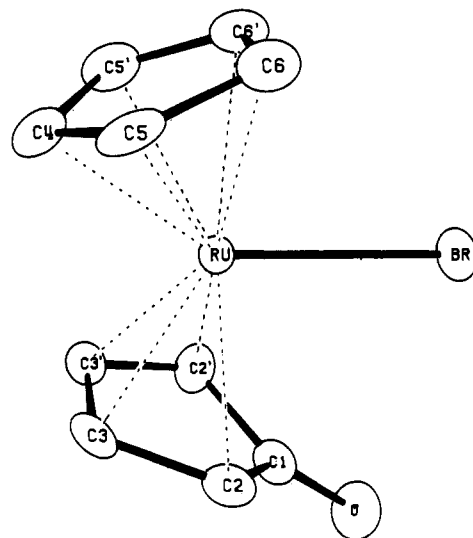


Figure 1. ORTEP diagram of Ru(cp)(cpO)Br.

HCl containing 4.00 g of FeCl<sub>3</sub> (hydrate). The two-phase mixture was stirred vigorously for 18 h. The acid layer was separated and washed with benzene and then ether. A 5-mL aqueous solution of 2.0 g of NH<sub>4</sub>PF<sub>6</sub> was added, and the solution was allowed to stand overnight, whereupon the crystalline solid that formed was collected. The yield was 62%.

[Ru(cp)<sub>2</sub>Br][PF<sub>6</sub>]. This complex was prepared in an analogous fashion, except that the oxidant was FeNH<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O in 3 M HBr. The yield was 90%.

[Ru(cp)(cpO)Cl]. A 0.10-g portion of [Ru(cp)<sub>2</sub>Cl]PF<sub>6</sub> was suspended in 5 mL of deionized H<sub>2</sub>O. The suspension was heated to 50 °C for 2 h and allowed to cool overnight. A colorless precipitate of Ru(cp)<sub>2</sub> together with red crystals were formed. The ruthenocene was extracted with three 5-mL portions of ether. The red crystals were collected and washed with acetone and then ether. The isolated yields were 30% Ru(cp)(cpO)Cl and 37% ruthenocene.

[Ru(cp)(cpO)Br]. This complex was prepared by the method used for the chloro analogue. The yields were 30% Ru(cp)(cpO)Br and 47% ruthenocene.

**X-ray Crystallography.** Data for a crystal of Ru(cp)(cpO)Br were collected on a PW 1100/20 Philips four-circle computer-controlled diffractometer. Mo K $\alpha$  ( $\lambda = 0.71069$  Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 25 reflections in the range  $12 < \theta < 15^\circ$ . Data were measured by using the  $\omega$ -2 $\theta$  method. The scan width,  $\Delta\omega$ , for each reflection was  $1^\circ$  with a scan time of 20 s. Background measurements were made at both limits of each scan. Crystallographic data and other pertinent information are presented in Table I. Lorentz and polarization corrections were applied. Intensity data were not corrected for absorption. The ruthenium atom was located by using the results of MULTAN direct-method analysis.<sup>11</sup> All other atoms were located in a series of difference Fourier maps. The structure was refined<sup>12</sup> in the space group *Pnma* to convergence.

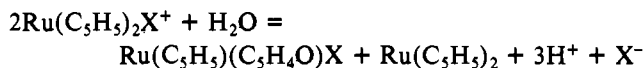
The discrepancy indices,  $R_1 = \sum[|F_o| - |F_c|]/\sum|F_o|$  and  $R_2 = [w(\sum|F_o - F_c|^2)/\sum|F_c|^2]^{1/2}$ , are listed in Table I. The final difference map showed no peaks of structural significance. Listings of observed and calculated structure factors are available as supplementary material. Table II lists the atomic position parameters and their corresponding esd's.

## Results

The description in the previous section of the preparation of the new complexes containing cyclopentadienone as a ligand on Ru(II) anticipated conclusions about their nature that were based on evidence now to be outlined.

The major products of the decomposition of the species Ru(cp)<sub>2</sub>Br<sup>+</sup> and Ru(cp)<sub>2</sub>Cl<sup>+</sup> are in each case ruthenocene, and

the putative respective cyclopentadienone complexes Ru(cp)(cpO)Br and Ru(cp)(cpO)Cl. These findings are consistent with the net change being



The oxidation of C<sub>5</sub>H<sub>5</sub><sup>-</sup> to



is a four-electron change so that the production of 1 mol of the ketone, at least in the absence of an external oxidant,<sup>13</sup> calls for 2 mol of Ru(IV).

The infrared spectrum of the new product isolated after the reaction of Ru(cp)<sub>2</sub>Br<sup>+</sup> with water shows a strong band at 1685 cm<sup>-1</sup>, which is in the region expected for a carbon-oxygen double bond.

The analysis of the X-ray diffraction data obtained for the bromo product fully confirms the conclusions about the nature of the new compound that were reached on the basis of the less direct evidence outlined above. An ORTEP drawing of Ru(cp)(cyclopentadienone)Br is shown in Figure 1.<sup>14</sup> Selected bond distances and bond angles are shown in Table III. The coordination number about the ruthenium can be considered to be 6. The average cyclopentadienyl-ring C-C distance is 1.42 Å, similar to those found in Ru(cp)<sub>2</sub> (1.43 Å) and Ru(cp)<sub>2</sub>I<sup>+</sup> (1.41 Å). The C-C distances found in the butadiene fragment of the cyclopentadienone group show the short-long-short pattern expected for a ground-state butadiene unit, and all the C-C distances are between those found for C-C single- and unconjugated double-bond lengths. The average metal-carbon bond length, excluding Ru-C(1) is 2.21 Å; this can be compared to the average Ru-C distances found in ruthenocene (2.21 Å)<sup>15</sup> and Ru(cp)<sub>2</sub>I<sup>+</sup> (2.20 Å).<sup>5</sup> The ruthenium-bromine distance is 2.556 Å; in [tris(*o*-(diphenylarsino)phenyl)arsine]ruthenium dibromide, it is 2.61 Å.<sup>16</sup>

- (11) Main, P.; Hull, S. E.; Lessinger, L.; German, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN 78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; Universities of York, England, and Louvain, Belgium, 1978.
- (12) All crystallographic computing was done on a CYBER 74 computer at the Hebrew University of Jerusalem using the SHELX-77 structure determination package.

- (13) It should be noted in passing that in the case of Ru(cp)<sub>2</sub>Br<sup>+</sup> the decomposition of the complex was carried out in the presence of Fe(III) with the result that the yield of the ketone product was increased and that of Ru(cp)<sub>2</sub> was decreased relative to those reported in the Experimental Section. The product distribution is the same when the reaction is run in the presence or absence of oxygen, and we conclude that the source of the ketone oxygen is water.
- (14) The chloro analogue is isostructural with the bromo complex. The unit cell dimensions are *a* = 13.721 (2) Å, *b* = 8.749 (1) Å, and *c* = 7.284 (1) Å.
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Table II. Positional Parameters and Estimated Standard Deviations

atom	x	y	z	atom	x	y	z
Ru	0.27284 (6)	0.25	0.4375 (1)	C(3)	0.1696 (5)	0.1680 (9)	0.240 (1)
Br	0.24415 (8)	0.25	0.7745 (1)	C(4)	0.3831 (8)	0.25	0.227 (2)
O	0.0237 (6)	0.25	0.615 (1)	C(5)	0.4004 (5)	0.120 (1)	0.335 (1)
C(1)	0.0845 (8)	0.25	0.496 (2)	C(6)	0.4226 (5)	0.169 (1)	0.508 (1)
C(2)	0.1314 (5)	0.118 (1)	0.406 (1)				

Table III. Selected Bond Lengths and Bond Angles

Bond Lengths (Å)			
Ru-Br	2.556 (1)	O-C(1)	1.22 (1)
-C(1)	2.60 (1)	C(1)-C(2)	1.49 (1)
-C(2)	2.263 (7)	C(2)-C(3)	1.42 (1)
-C(3)	2.167 (7)	C(3)-C(3)'	1.46 (1)
-C(4)	2.17 (1)	C(4)-C(5)	1.43 (1)
-C(5)	2.222 (7)	C(5)-C(6)	1.40 (1)
-C(6)	2.223 (7)	C(6)-C(6)'	1.44 (1)
Angles (deg)			
Br-Ru-C(1)	71.6 (3)	C(3)-Ru-C(4)	87.1 (3)
-C(2)	88.4 (2)	-C(5)	95.3 (3)
-C(3)	125.3 (2)	-C(6)	130.3 (3)
-C(4)	145.2 (3)	-C(3)'	39.3 (3)
-C(5)	117.5 (2)	-C(5)'	116.3 (3)
-C(6)	84.5 (2)	-C(6)'	149.8 (3)
C(1)-Ru-C(2)	34.9 (2)	C(4)-Ru-C(5)	37.9 (3)
-C(3)	58.4 (3)	-C(6)	62.7 (4)
-C(4)	143.2 (4)	C(5)-Ru-C(6)	36.8 (3)
-C(5)	145.8 (2)	-C(5)'	62.7 (3)
-C(6)	149.6 (3)	-C(6)'	62.4 (3)
C(2)-Ru-C(3)	37.4 (3)	C(6)-Ru-C(6)'	37.9 (3)
-C(4)	120.7 (3)	O-C(1)-C(2)	128.3 (5)
-C(5)	111.0 (3)	C(2)-C(1)-C(2)'	103.4 (8)
-C(6)	129.4 (3)	C(1)-C(2)-C(3)	107.8 (7)
-C(2)'	62.3 (3)	C(2)-C(3)-C(3)'	108.1 (7)
-C(3)'	63.5 (3)	C(5)-C(4)-C(5)'	108.1 (1)
-C(5)'	153.6 (3)	C(4)-C(5)-C(6)	107.9 (8)
-C(6)'	166.0 (3)	C(5)-C(6)-C(6)'	108.0 (7)

Both C(1) and O are out of the plane of the butadiene unit and away from the metal center. The angle between the line formed by the CO group and the butadiene plane is 20.6°. In other cyclopentadienone and substituted cyclopentadienone complexes the CO is also bent away from the metal.<sup>17</sup> Unlike Ru(cp)<sub>2</sub> and Ru(cp)<sub>2</sub>I<sup>+</sup> the rings have adopted a staggered conformation. The dihedral angle 36.2° formed by the intersection of the planes defined by the cyclopentadienide and cyclopentadienone is similar to that found in Ru(cp)<sub>2</sub>I<sup>+</sup> (32.2°).

The cyclopentadienone species were further characterized by measuring the proton NMR spectra. That of the chloro product shows two multiplets centered at δ 6.01 and 4.18 and a singlet at δ 5.47. For the bromo species, these features appear at δ 6.14, 4.28, and 5.51, respectively. The high-field multiplet is assigned to the C(3) protons, the low-field multiplet to C(2) protons, and the singlet to cp protons.<sup>18</sup>

In the course of the investigation, additional qualitative observations on the reactions of the Ru(IV) species were made, which are herewith outlined. The trihalo salts [Ru(cp)<sub>2</sub>X]X<sub>3</sub> (X = Cl, Br, I) are only sparingly soluble in water. So as to

increase the solubility and to avoid complications that might arise from the reactions of X<sub>3</sub><sup>-</sup>, we prepared salts with Cl<sub>3</sub><sup>-</sup> and Br<sub>3</sub><sup>-</sup> replaced by PF<sub>6</sub><sup>-</sup>. The PF<sub>6</sub><sup>-</sup> salts persist in strong aqueous acid and in rigorously dried dichloromethane, acetonitrile, or nitromethane, but they decompose in acetone or dimethyl sulfoxide even when these solvents are rigorously dried. The decomposition in aqueous alkali is more rapid than in water alone, and the cyclopentadienone complex and ruthenocene have been shown to be among the eventual products. There are indications in the case of aqueous alkali as the reaction medium that the initial rapid reaction produces an intermediate, which then decomposes at a rather slow rate (several hours).

### Discussion

Unsubstituted cyclopentadienone is unstable, and it is understandable that not many complexes of the simple ligand are described in the literature. The ligand has been assembled on a metal from acetylene and carbon monoxide,<sup>19</sup> but to our knowledge the formation of a complex by the oxidation of a coordinated cyclopentadiene anion has hitherto not been reported.

Comparisons of the structural parameters we have outlined with those reported for other cyclopentadienone complexes are not particularly revealing because the other structure determinations have been done with derivatives. It is worth noting that the lengthening of the C(3)-C(3)' distance relative to C(2)-C(3) expected for the orthodox bond distribution in the molecule is clearly revealed in data summarized in Table III. This feature is not always apparent in the related structural work.

The motivation for the work described here was to explore the aquo chemistry of Ru<sup>IV</sup>(cp)<sub>2</sub> in the expectation that species such as Ru(cp)<sub>2</sub>OH<sup>+</sup> and Ru(cp)<sub>2</sub>O would exist (the former is the direct analogue to Ru(cp)<sub>2</sub>X<sup>+</sup>). Our experience indicates that the aquo or hydroxo derivatives of Ru<sup>IV</sup>(cp)<sub>2</sub> are unstable. Such species may be present in the solid first formed when Ru(cp)<sub>2</sub>Br<sup>+</sup> is added to aqueous alkali, but it is more likely that the OH<sup>-</sup> first attacks one of the rings rather than replacing Br<sup>-</sup> on the metal.

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**Registry No.** [Ru(cp)<sub>2</sub>Cl]Cl<sub>3</sub>, 90109-02-7; [Ru(cp)<sub>2</sub>Cl][PF<sub>6</sub>], 90109-03-8; [Ru(cp)<sub>2</sub>Br][PF<sub>6</sub>], 90109-04-9; Ru(cp)(cpO)Cl, 90109-05-0; Ru(cp)(cpO)Br, 90109-06-1; Ru(cp)<sub>2</sub>, 1287-13-4.

**Supplementary Material Available:** Listings of anisotropic thermal parameters and observed and calculated structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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