*Inorg. Chem.* **2003**, *42*, 5480–5482

Inorganic Chemistry
Communication

# Electrochemical Preparation of the Bis(ruthenocenium) Dication

**Sabrina Trupia, Ayman Nafady, and William E. Geiger***

*Department of Chemistry, University of Vermont, Burlington, Vermont 05405*

Received May 1, 2003

The electrochemical oxidation of ruthenocene (**1**) in $CH_2Cl_2$/[$NBu_4$]A, where A = $[B(C_6F_5)_4]^-$ or $[B(C_6H_3(CF_3)_2)_4]^-$, gives the dimeric dication $[(RuCp_2)_2]^{2+}$, $\mathbf{2}^{2+}$, in equilibrium with the 17-electron ruthenocenium ion $\mathbf{1}^+$. At room temperature the rapid equilibrium accounts for the quasi-Nernstian cyclic voltammetry (CV) behavior ($E_{1/2}$ = 0.41 V vs $FeCp_2$, A = $[B(C_6F_5)_4]^-$). Direct electrochemical evidence for $\mathbf{2}^{2+}$ is seen by CV and by bulk electrolysis at 243 K. The bis(ruthenocenium) dication undergoes a highly irreversible two-electron cathodic reaction at $E_{pc}$ ca. 0 V. Anodic electrolysis of **1** at 243 K using $[B(C_6H_3(CF_3)_2)_4]^-$ as the supporting electrolyte, followed by cathodic electrolysis of $\mathbf{2}^{2+}$, regenerates half of the original **1**. Precipitation of $\mathbf{2}^{2+}$ occurs when the supporting electrolyte is $[B(C_6F_5)_4]^-$, allowing facile isolation of $[(RuCp_2)_2][B(C_6F_5)_4]_2$. A second, unidentified, anodic product also reduces to give back ruthenocene. Digital simulations of the CV curves of **1** at 243 K give a dimerization equilibrium constant of $9 \times 10^4$ $M^{-1}$ for $K_{eq} = [(RuCp_2)_2{}^{2+}]/2\ [RuCp_2]^+$ in $CH_2Cl_2$/0.1 M $[NBu_4][B(C_6F_5)_4]$.

Compared to the simplicity of the oxidation of ferrocene, that of ruthenocene, $RuCp_2$ (Cp = $\eta^5$-$C_5H_5$), is complex and still not well understood. Hill et al.[1] reported the first electrolyte conditions, namely, $CH_2Cl_2$/0.1 M $[NBu_4][B(C_6H_3(CF_3)_2)_4]$, in which ruthenocene undergoes an apparently reversible one-electron oxidation to $[RuCp_2]^+$, $\mathbf{1}^+$ (eq 1). A

$$\mathrm{RuCp_2} \rightleftharpoons [\mathrm{RuCp_2}]^+ + e^- \tag{1}$$

number of earlier studies had found that the oxidation of **1** results in products that vary with the nature of the medium, most likely owing to disproportionation reactions involving the primary oxidation products with added or adventitious nucleophiles.[2] It has been postulated in several papers that the bis(ruthenocenium) dication $[RuCp_2]_2{}^{2+}$, $\mathbf{2}^{2+}$, may play a role in the redox process,[1,3,4] but there is no published experimental evidence to this effect. In the present communication we report cyclic voltammetry (CV) and bulk electrolysis data in $CH_2Cl_2$/0.1 M $[NBu_4]$A, where A is either the tetrakis(perfluoroaryl)borate (TFAB) anion[5] $[B(C_6F_5)_4]^-$ or $[B(C_6H_3(CF_3)_2)_4]^-$, which give the first experimental verification of $\mathbf{2}^{2+}$. The dimer dication is favored over the monomer monocation under these conditions (eq 2, $K_{eq} > 1$), requiring that the role of $\mathbf{2}^{2+}$ be taken into account in oxidative reactions of **1**.

$$2[\mathrm{RuCp_2}]^+ \rightleftharpoons [(\mathrm{RuCp_2})_2]^{2+} \qquad K_{eq} = k_{dim}/k_{mon} \tag{2}$$

Ruthenocene undergoes a one-electron oxidation having a quasi-Nernstian CV shape in $CH_2Cl_2$ containing 0.1 M $[NBu_4]$[TFAB], analogous to the behavior reported earlier for **1** in 0.1 M $[NBu_4][B(C_6H_3(CF_3)_2)_4]$.[1] No qualitative change in behavior was observed at room temperature over a substrate concentration range of 0.2−5.2 mM at a scan rate of 0.1 V $s^{-1}$ (Figure S1 in Supporting Information). An $E_{1/2}$ value of 0.41 V vs $FeCp_2$ is estimated[6,7] for $[RuCp_2]^{0/+}$. At reduced temperatures the oxidation displays decreased electrochemical reversiblity[8] and a new cathodic wave for a reaction product, ascribed to $\mathbf{2}^{2+}$, is observed (Figure 1). This product wave has a broad and electrochemically irreversible shape for which the peak potential (−0.06 V vs $FeCp_2$ at $\nu$ = 0.2 V $s^{-1}$, $T$ = 243 K) is dependent on scan rate, temperature, supporting electrolyte anion, and substrate

---

* Author to whom correspondence should be addressed. E-mail: wgeiger@zoo.uvm.edu.

(1) Hill, M. G.; Lamanna, W. M.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 4687.

(2) (a) Bublitz, D. E.; Hoh, G.; Kuwana, T. *Chem. Ind. (London)* **1959**, 635. (b) Kuwana, T.; Bublitz, D. E.; Hoh, G. *J. Am. Chem. Soc.* **1960**, *82*, 5811. (c) Gubin, S. P.; Smirnova, S. A.; Denisovich, L. I.; Lubovich, A. A. *J. Organomet. Chem.* **1971**, *30*, 243. (d) Denisovich, L. I.; Zakurin, N. V.; Bezrukova, A. A.; Gubin, S. P. *J. Organomet. Chem.* **1974**, *81*, 207. (e) See also: Kukharenko, S. V.; Strelets, V. V.; Kudinov, A. R.; Kreidlin, A. Z.; Peterleitner, M. G.; Denisovich, L. I.; Rybinskaya, M. I. *J. Organomet. Chem.* **1996**, *519*, 1.

(3) Droege, M. W.; Harman, W. D.; Taube, H. *Inorg. Chem.* **1987**, *26*, 1309.

(4) Inam-ul-Haque; Iqbal, S. *Sci. Int. (Lahore)* **2001**, *13*, 49 (CAN 135: 217544.

(5) LeSuer, R. J.; Geiger, W. E. *Angew. Chem., Int. Ed.* **2000**, *39*, 248.

(6) The measured $E_{1/2}$ is slightly dependent on concentration of $RuCp_2$, as expected for a redox process with a coupled reversible equilibrium. The $E_{1/2}$ of 0.41 V refers to a concentration of 1 mM **1** in 0.1 M $[NBu_4][B(C_6F_5)_4]$. A negative potential shift is observed as the concentration increases, consistent with an EC mechanism in which the chemical reaction is fast and reversible. For introduction to EC mechanisms, see: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd ed.; John Wiley and Sons: New York, 2001; p 473.

(7) The literature value[1] for 0.5 mM **1** in $CH_2Cl_2$/0.1 M $[NBu_4][B(C_6H_3(CF_3)_2)_4]$ of 0.56 V at room temperature was confirmed by independent measurements. Our measured value for 5 mM **1** in $CH_2Cl_2$/0.05 M $[NBu_4][B(C_6H_3(CF_3)_2)_4]$ is 0.57 V at 243 K. The $E_{1/2}$ values are decidedly more negative with $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte.

(8) The reverse-to-forward current ratios for the $[RuCp_2]^{0/+}$ wave varied from 0.4 (i.e., chemically irreversible) at $\nu$ = 0.05 V $s^{-1}$ to 0.8 at $\nu$ = 1 V $s^{-1}$, $T$ = 243 K.

10.1021/ic030146+ CCC: $25.00

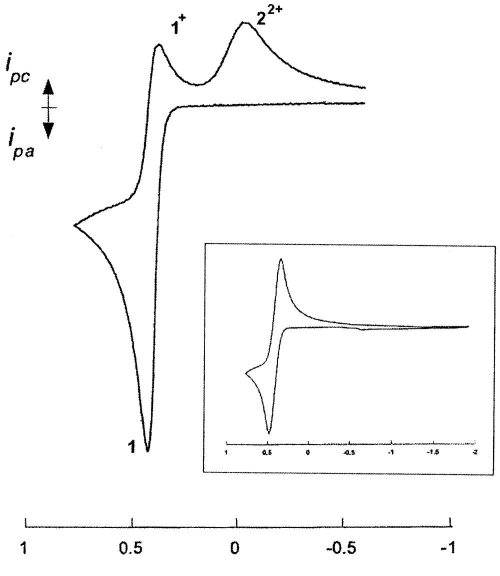


**Figure 1.** Cyclic voltammogram of 2 mM $RuCp_2$ in $CH_2Cl_2$/0.1 M $[NBu_4][B(C_6F_5)_4]$ at 2 mm ($d$) glassy carbon electrode, $T = 243$ K, $\nu = 0.2$ V $s^{-1}$. Inset gives scan under same conditions at ambient temperature.

concentration. At subambient temperatures, increasing concentrations lead to diminished reversibility for the $[RuCp_2]^{0/+}$ couple and a more dominant contribution from the wave for $\mathbf{2}^{2+}$ (Figure S2 in Supporting Information).

The voltammetry is consistent with the $EC_{dim}$ mechanism of eqs 1 and 2, in which the chemical reaction following electron transfer is the dimerization of the ruthenocenium ion to give the bis(ruthenocenium) dication $[(RuCp_2)_2]^{2+}$, $\mathbf{2}^{2+}$.[9,10] Reduction of the latter occurs in an electrochemically irreversible net two-electron cathodic process ($E_{pc}$ ca. 0 V)[11] to regenerate neutral ruthenocene (eq 3).

$$[(RuCp_2)_2]^{2+} + 2e^- \rightarrow 2RuCp_2 \qquad (3)$$

The long-term stability and isolation of the dimer dication was addressed by bulk electrolysis of 5 mM $RuCp_2$ at a platinum basket electrode. At room temperature a green solution was produced with a coulomb count in excess of 1.2 F/equiv. Discontinuing the electrolysis resulted in a rapid color change to red. Subsequent CV scans showed the presence of several products, including $\mathbf{2}^{2+}$. An essentially identical result was obtained with benzotrifluoride[12] as the solvent.

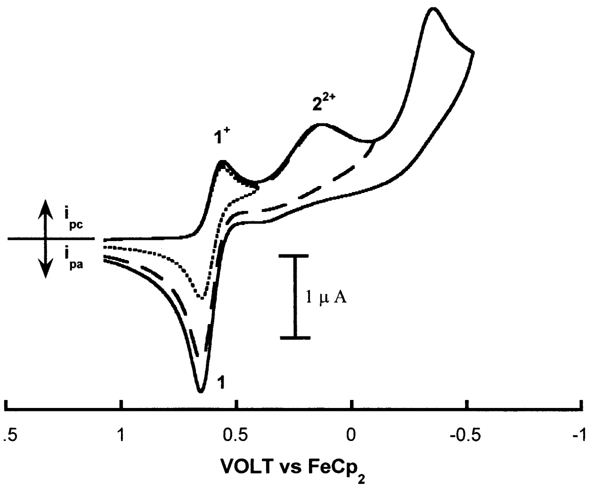


**Figure 2.** Cyclic voltammograms to three different switching potentials after anodic oxidation of 5 mM ruthenocene in $CH_2Cl_2$/0.05 M $[NBu_4][B(C_6H_3(CF_3)_2)_4]$ at 243 K, 1 mm glassy carbon electrode, 0.1 V $s^{-1}$.

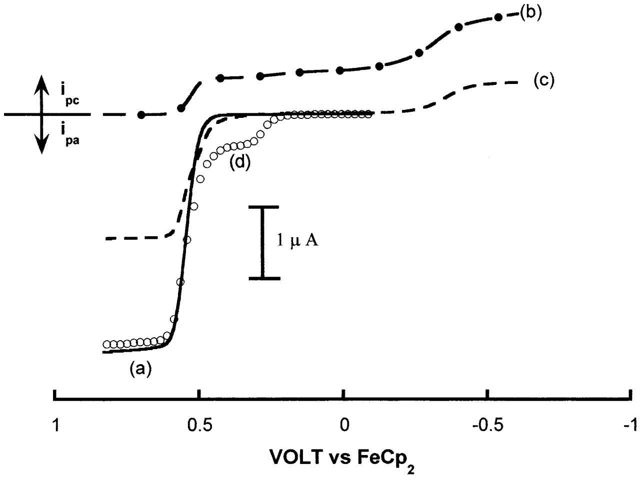


**Figure 3.** Linear scan voltammograms obtained during electrolysis experiments on 5 mM ruthenocene in $CH_2Cl_2$/0.05 M $[NBu_4][B(C_6H_3(CF_3)_2)_4]$ at 243 K, 1 mm glassy carbon electrode, 3 mV $s^{-1}$ scan rate: (—) (a) initial solution; (—•—•) (b) after anodic electrolysis at $E_{appl} = 0.8$ V; (- - -) (c) after cathodic re-electrolysis at $E_{appl} = -0.12$ V; (○) (d) after final cathodic re-electrolysis at $E_{appl} = -0.65$ V.

The anodic reaction was simplified by electrolysis at lower temperatures. At 243 K a precise coulometry of 1 F/equiv was observed in either dichloromethane or benzotrifluoride. When the electrolyte anion was TFAB, a light yellow precipitate formed, which was filtered off in good yield. It gave an elemental analysis[13] consistent with $[(RuCp_2)_2][B(C_6F_5)_4]_2$ and an IR feature ($\nu_{CH(bend)}$, 846 $cm^{-1}$) consistent with ruthenocenium moieties.[14] X-ray quality crystals of $\mathbf{2}^{2+}$ have not yet been obtained. The major remaining CV feature of the electrolysis solution was an irreversible cathodic peak at −0.3 V to −0.4 V depending on electrolyte, due to what we refer to as a secondary product (Figure 2). When the electrolyte anion was $[B(C_6H_3(CF_3)_2)_4]^-$, no precipitation was observed. The olive-colored solution had CV and linear scan voltammetry (LSV) features characteristic of both the $\mathbf{1}^+ + \mathbf{2}^{2+}$ mixture and the secondary product (Figures 2 and 3). Cathodic re-electrolysis at $E_{appl} = -0.12$ V regenerated ca.

---

(9) An alternative mechanism is one in which $\mathbf{1}^+$ reacts with **1** to form the dimer *monocation* $\mathbf{2}^+$, which then undergoes oxidation to the dication $\mathbf{2}^{2+}$. For more on radical−radical vs radical−substrate dimerization mechanisms, see ref 10.

(10) (a) Nadjo, L.; Savéant, J. M. *J. Electroanal. Chem.* **1971**, *33*, 419; (b) **1973**, *44*, 327. (c) Amatore, C.; Garreau, D.; Hammi, M.; Pinson, J.; Savéant, J. M. *J. Electroanal. Chem.* **1985**, *184*, 1. (d) Crooks, R. M.; Bard, A. J. *J. Electroanal. Chem.* **1988**, *240*, 253.

(11) At $\nu = 0.2$ V $s^{-1}$, $E_{pc} = -0.06$ V in $CH_2Cl_2/[NBu_4][B(C_6F_5)_4]^-$ and 0.13 V in $CH_2Cl_2/[NBu_4][B(C_6H_3(CF_3)_2)_4]$.

(12) Ohrenberg, C.; Geiger, W. E. *Inorg. Chem.* **2000**, *39*, 2948.

(13) Elemental analysis (Robertson Laboratories): C, 43.74% (calcd 44.79%); H, 1.20% (calcd 1.10%).

(14) Nujol mull spectra of **1** have a band at 806 $cm^{-1}$ assigned to $\nu_{CH(bend)}$ which increases by 40 $cm^{-1}$ to 846 $cm^{-1}$ for $\mathbf{2}^{2+}$. A similar shift has been assigned to $\nu_{CH(bend)}$ in ferrocene/ferrocenium (Kramer, J. A.; Hendrickson, D. N. *Inorg. Chem.* **1980**, *19*, 3330). We measure 815 $cm^{-1}$ for ferrocene and 855 $cm^{-1}$ for $[FeCp_2][B(C_6F_5)_4]$ under identical sample conditions.

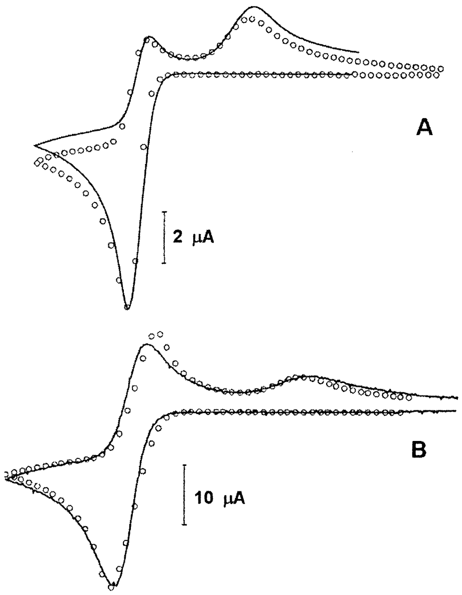
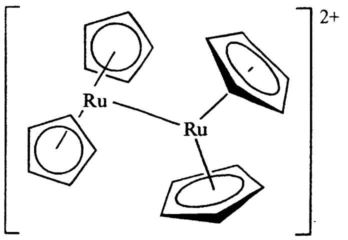


**Figure 4.** Comparison of CV experiment (—) and simulations (○) for 1 mM $RuCp_2$, $T = 243$ K, at two different scan rates: A, $\nu = 0.2$ V $s^{-1}$; B, $\nu = 1$ V $s^{-1}$. Pertinent simulation parameters: $\mathbf{1}/\mathbf{1}^+$, $E° = 0.41$ V; $k_s = 1$ cm $s^{-1}$; $\alpha = 0.5$; $\mathbf{2}^{2+}/\mathbf{2}^+$, $E° = 0.30$ V; $k_s = 1 \times 10^{-5}$ cm $s^{-1}$; $\alpha = 0.4$; $\mathbf{2}^+/\mathbf{2}$, $E° = 0.37$; $k_s = 0.1$; $\alpha = 0.5$.

50% **1** through reduction of the mixture of $\mathbf{1}^+$ and $\mathbf{2}^{2+}$. Re-electrolysis at $E_{\text{appl}} = -0.65$ V, involving also the reduction of the secondary product, increased the regeneration of ruthenocene to 84% and produced another small wave with $E_{1/2} = 0.29$ V. Reduction of the secondary product, which on the basis of previous literature[15] is likely to be a Ru(IV) species, is therefore seen to mainly regenerate ruthenocene.

On the basis of analogy to the structurally characterized[3] osmium analogue, $\mathbf{2}^{2+}$ is likely to have Cp rings that are tilted away from the Ru−Ru bond and rotated with respect to each other (90° in $[(OsCp_2)_2][PF_6]_2$) in order to minimize steric repulsions.[16]



Proposed Structure of $[(RuCp_2)_2]^{2+}$

Digital simulations[17] help to delineate the ruthenocene oxidation mechanism. Figure 4 compares simulated and experimental curves employing $EC_{\text{dim}}$ for the anodic process (eqs 1 and 2, $K_{\text{eq}} = 9 \times 10^4$ $M^{-1}$; $k_{\text{dim}} = 6.5 \times 10^2$ $M^{-1}$ $s^{-1}$) and $E_{\text{irrev}}E$ for the cathodic process (conditions: 1 mM ruthenocene at 243 K). The general shape and behavior of the cathodic wave is consistent with a two-electron process (eq 3) in which the first electron transfer is the rate-limiting step.[18] Neither the rates nor the $E_{1/2}$ values of the two-electron *cathodic* process are precisely determined by the simulations, which can be fit with experiment using ranges of values. Similarly shaped CV curves have been observed for a number of other dimetallic compounds in which reduction gives facile metal−metal bond cleavage.[19] It is reported that the osmium analogue $[(OsCp_2)_2]^{2+}$ reduces with re-formation of $OsCp_2$ upon reduction.[20]

As expected on the basis of previous literature,[1,2] addition of $[PF_6]^-$ or $[BF_4]^-$ to solutions of **1** in $CH_2Cl_2/[NBu_4][TFAB]$ has a dramatic effect on the oxidation process. Even substoichiometric amounts of $[PF_6]^-$ decrease the chemical reversibility of $[RuCp_2]^{0/+}$ without evidence for the formation of the dimer (Figure S3, Supporting Information). The rapid reaction between $[RuCp_2]^+$ and $[PF_6]^-$ is likely to involve a formal Ru(IV) complex such as $[Ru(F\text{-}PF_5)Cp_2]^+$. Analogous complexes of the type $[RuCp_2X]^+$, where X = halide, have been isolated.[21]

Results to date may be summarized as follows. In a medium containing solvents of low donor strength and anions of weak nucleophilicity, the oxidation of **1** gives 17-electron $\mathbf{1}^+$ in equilibrium with the dominant dimer dication $\mathbf{2}^{2+}$. When the supporting electrolyte anion is TFAB, the dimer precipitates at 243 K, giving the light-yellow $[(RuCp_2)_2][B(C_6F_5)_4]_2$. To our knowledge, this is only the second confirmed report of an unbridged metal−metal bonded metallocene, the precursor being the osmium analogue.[3] Using $[B(C_6H_3(CF_3)_2)_4]^-$ as the electrolyte anion avoids the precipitation[22] and enhances the formation of a yet unidentified secondary product which may be reduced back to ruthenocene. These findings should contribute to more systematic studies of the oxidative chemistry of ruthenocene, its derivatives, and its analogues.

**Acknowledgment.** The authors are grateful for the support of this work by the National Science Foundation (CHE -0092702). We also thank the Egyptian Cultural & Educational Bureau for support of A.N.

**Supporting Information Available:** Three figures (S1−S3) of voltammograms describing experimental results given in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

IC030146+

---

[15] Bruce, M. I. In *Comprehensive Organometallic Chemistry II*; Shriver, D. F., Bruce, M. I., Eds.; Pergamon Press: New York, 1995; Vol. 7, pp 608−609.

[16] The van der Waals radii of ruthenium and osmium are similar.

[17] Digital simulations were carried out using Digisim 3.03 (Bioanalytical Systems).

[18] Ryan, M. D. *J. Electrochem. Soc.* **1978**, *125*, 547.

[19] (a) Richards, T. C.; Geiger, W. E.; Baird, M. C. *Organometallics* **1994**, *13*, 4494. (b) Tenhaeff, S. C.; Covert, K. J.; Castellani, M. P.; Grunkemeier, J.; Kunz, C.; Weakley, T. J. R.; Koenig, T.; Tyler, D. R. *Organometallics* **1993**, *12*, 5000. (c) Pugh, J. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 3784. (d) Fortier, S.; Baird, M. C.; Preston, K. F.; Morton, J. R.; Ziegler, T.; Jaeger, T. J.; Watkins, W. C.; MacNeil, J. H.; Watson, K. A.; Hensel, K.; LePage, Y.; Charland, J.-P.; Williams, A. J. *J. Am. Chem. Soc.* **1991**, *113*, 542.

[20] Kukharenko, S. V.; Bezrukova, A. A.; Rubezhov, A. Z.; Strelets, V. V. *Metalloorg. Khim.* **1990**, *3*, 634 (electrochemistry of osmocene in low-temperature THF).

[21] (a) Sohn, Y. S.; Schlueter, A. W.; Hendrickson, D. N.; Gray, H. B. *Inorg. Chem.* **1974**, *13*, 301. (b) Kirchner, K.; Dodgen, H. W.; Wherland, S.; Hunt, J. P. *Inorg. Chem.* **1990**, *29*, 2381 and references therein.

[22] The high solubility in nonaqueous solvents of salts containing $[B(C_6H_3(CF_3)_2)_4]^-$ is well-known. See: Brookhart, M.; Liu, Y.; Goldman, E. W.; Timmers, D. A.; Williams, G. D. *J. Am. Chem. Soc.* **1991**, *113*, 927.