

Direct Observation of Ligand-Centered Redox in  $\text{Cp}^*\text{Rh}_2(\mu\text{-C}_2\text{S}_4)\text{Cl}_x$  ( $x = 2, 0$ )<sup>†</sup>

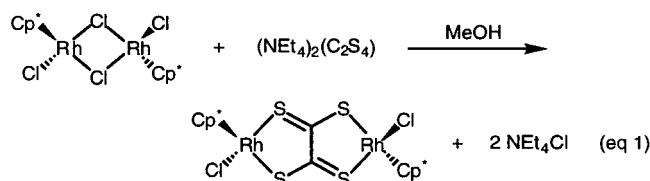
Geoffrey A. Holloway and Thomas B. Rauchfuss\*

School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

Received February 4, 1999

The coordination chemistry of tetrathiooxalate (tto) has received intermittent attention for two decades.<sup>1–10</sup> Complexes of this ligand occur in a range of oxidation states, the limits of which can be described as  $\text{C}_2\text{S}_4^{2-}$  ( $r_{\text{C-C}} \sim 1.46 \text{ \AA}$ )<sup>11</sup> and  $\text{C}_2\text{S}_4^{4-}$  ( $r_{\text{C-C}} \sim 1.35 \text{ \AA}$ ).<sup>1</sup> Thus, somewhat like NO and SO<sub>2</sub>, C<sub>2</sub>S<sub>4</sub> is a facultative ligand with the capability of absorbing or releasing redox equivalents. Unlike SO<sub>2</sub> and NO, however, C<sub>2</sub>S<sub>4</sub> is strictly binucleating.<sup>1–10</sup> This combination of properties—electronically facultative and binucleating—is of interest in the design of functional multimetallic ensembles wherein ligands contribute to the redox properties of pairs of metals. In this report we demonstrate that both the metal and the C<sub>2</sub>S<sub>4</sub> subunits participate in the redox cycle of an M<sub>2</sub>C<sub>2</sub>S<sub>4</sub> unit. This work should stimulate further studies on the coordination chemistry of C<sub>2</sub>S<sub>4</sub><sup>2-</sup>, for which an alternative synthesis recently has been reported.<sup>12</sup>

Treatment of methanol slurries of  $[\text{Cp}^*\text{RhCl}_2]_2$  with  $(\text{NEt}_4)_2\text{C}_2\text{S}_4$  efficiently affords the new compound  $[\text{Cp}^*\text{RhCl}]_2(\mu\text{-C}_2\text{S}_4)$  (**1**·Cl<sub>2</sub>) (eq 1).<sup>13</sup> Spectroscopic and crystallographic analyses of this



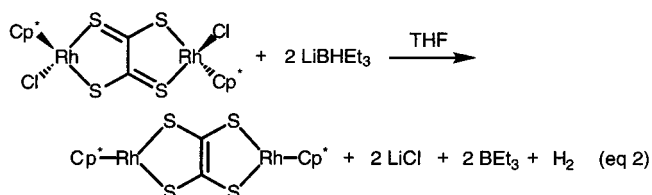
dark green material established a transoid C<sub>2h</sub> structure (Figure

<sup>†</sup> This paper is dedicated to Professor H. Werner on the occasion of his 65th birthday.

- (1) Maj, J. J.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1982**, *104*, 4278–4280.
- (2) Broadhurst, P. V.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1982**, 140–141.
- (3) Hansen, L. K.; Sieler, J.; Strauch, P.; Dietzsch, W.; Hoyer, E. *Acta Chem. Scand.* **1985**, *A39*, 571–591.
- (4) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M.; Zanello, P. *J. Am. Chem. Soc.* **1987**, *109*, 185–198.
- (5) Harris, H. A.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1987**, *109*, 4739–4741.
- (6) Vicente, R.; Ribas, J.; Alvarez, S.; Segui, A.; Solans, X.; Verdaguier, M. *Inorg. Chem.* **1987**, *26*, 4004–4009.
- (7) Reynolds, J. R.; Lillya, C. P.; Chien, J. C. W. *Macromolecules* **1987**, *20*, 1184–1191.
- (8) Yang, X.; Doxsee, D. D.; Rauchfuss, T. B.; Wilson, S. R. *J. Chem. Soc., Chem. Commun.* **1994**, 821–822.
- (9) Pullen, A. E.; Zeltner, S.; Olk, R. M.; Hoyer, E.; Abboud, K. A.; Reynolds, J. R. *Inorg. Chem.* **1996**, *35*, 4420–4426.
- (10) Pullen, A. E.; Zeltner, S.; Olk, R. M.; Hoyer, E.; Abboud, K. A.; Reynolds, J. R. *Inorg. Chem.* **1997**, *36*, 4163–4171.
- (11) Lund, H.; Hoyer, E.; Hazell, R. G. *Acta Chem. Scand.* **1982**, *B36*, 207–209.
- (12) Breitzer, J. G.; Chou, J.-H.; Rauchfuss, T. B. *Inorg. Chem.* **1998**, *37*, 2080–2083.
- (13)  $[\text{Cp}^*\text{RhCl}]_2(\text{C}_2\text{S}_4)$  (**1**·Cl<sub>2</sub>). To a stirred slurry of 0.22 g (0.36 mmol) of  $[\text{Cp}^*\text{RhCl}_2]_2$  in 20 mL of MeOH was added a solution of 0.17 g (0.40 mmol) of  $(\text{NEt}_4)_2(\text{C}_2\text{S}_4)$ <sup>12</sup> in 20 mL of MeOH. The slurry immediately turned from red-orange to dark green; after ~1 min, much precipitation appeared. After 5 min, solvent was removed under reduced pressure. The dark green solid was washed with 30 mL of H<sub>2</sub>O, 2 × 15 mL of MeOH, and 2 × 10 mL of Et<sub>2</sub>O and dried in air. Yield: 0.19 g (76%). Anal. Calcd (found) for C<sub>22</sub>H<sub>30</sub>S<sub>4</sub>Cl<sub>2</sub>Rh<sub>2</sub>: C, 37.78 (37.48); H, 4.37 (4.32). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 1.73 (Me<sub>5</sub>C<sub>5</sub>). <sup>13</sup>C NMR (150 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 9.33 (Me<sub>5</sub>C<sub>5</sub>), 100.27 (Me<sub>5</sub>C<sub>5</sub>, J<sub>Rh-C</sub> 6.9 Hz), 234.71 (C<sub>2</sub>S<sub>4</sub>). UV–vis (CH<sub>2</sub>Cl<sub>2</sub>): 340, 446, 656 nm.

1). The S<sub>2</sub>C–CS<sub>2</sub> distance of 1.447(13) Å is consistent with the C<sub>2</sub>S<sub>4</sub><sup>2-</sup> formulation, i.e.,  $[\text{Cp}^*\text{Rh}^{\text{III}}\text{Cl}]_2(\mu\text{-C}_2\text{S}_4^{-\text{II}})$ . The intense green color is ascribed to a low-energy Rh-to-C<sub>2</sub>S<sub>4</sub> charge-transfer transition. We also prepared the analogue  $[\text{Cp}^*\text{IrCl}]_2(\mu\text{-C}_2\text{S}_4)$  (**2**·Cl<sub>2</sub>), whereas  $[(\text{C}_6\text{R}_6)\text{RuCl}]_2(\mu\text{-C}_2\text{S}_4)$  has not yet been isolated in pure form. Many of the previous examples of organometallic C<sub>2</sub>S<sub>4</sub> complexes were prepared by the reductive coupling of CS<sub>2</sub>,<sup>1,2,4,5</sup> as opposed to the direct metathesis reaction reported here.

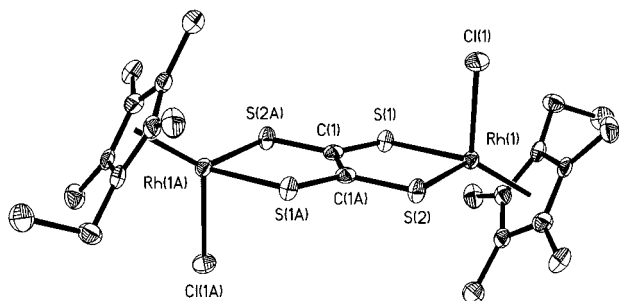
Treatment of a THF suspension of **1**·Cl<sub>2</sub> with LiBHET<sub>3</sub> or Na-(Hg) affords blue  $[\text{Cp}^*\text{Rh}]_2(\mu\text{-C}_2\text{S}_4)$  (**1**) (eq 2), a diamagnetic compound.<sup>14</sup> This reaction has been extended to the analogous Ir



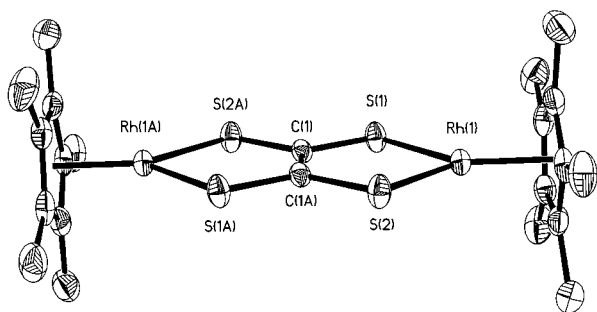
complex (**2**), which is also diamagnetic. Crystallographic analysis established that the Rh<sub>2</sub>C<sub>2</sub>S<sub>4</sub> core in **1** has D<sub>2h</sub> symmetry (Figure 2). The diamagnetism of **1** and **2** is of interest because the 1e<sup>-</sup>/M redox process should generate a [d<sup>7</sup>]<sub>2</sub> product. The diamagnetism of these species could be explained if the metals were strongly coupled through the π-system of the C<sub>2</sub>S<sub>4</sub> bridge so that the ground electronic state would not be describable in terms of isolated monometallic units. This convenient conclusion appears to be incorrect. The structural analysis shows that the S<sub>2</sub>C–CS<sub>2</sub> distance in **1** is 0.1 Å shorter than that in **1**·Cl<sub>2</sub> (1.342(8) vs 1.447(13) Å, respectively); thus, reduction strongly affects the oxidation state of the C<sub>2</sub>S<sub>4</sub> ligand. In other words, the structural data show that the redox process is best described as  $[\text{Cp}^*\text{Rh}^{\text{III}}\text{Cl}]_2(\mu\text{-C}_2\text{S}_4^{-\text{II}})$  to  $[\text{Cp}^*\text{Rh}^{\text{III}}]_2(\mu\text{-C}_2\text{S}_4^{-\text{IV}})$ . From this perspective, the metal centers in **1** more closely resemble those in Rh<sup>III</sup> dithiolates, e.g., Cp<sup>\*</sup>Rh(SC<sub>6</sub>F<sub>4</sub>-p-H)<sub>2</sub>.<sup>15</sup> Compound **1** behaves like a saturated Rh(III) derivative in the sense that it does not bind Lewis bases, including CO. Although formally unsaturated, the Rh centers in **1** are stabilized by S-to-metal π-bonding, as observed in the aforementioned Rh dithiolato complex and Cp<sup>\*</sup>-Ir<sub>2</sub>(μ-S)<sub>2</sub>(PMe<sub>3</sub>).<sup>16</sup>

Treatment of **1** with 1 equiv of Cl<sub>2</sub> regenerates **1**·Cl<sub>2</sub>. Under mild conditions, the Rh<sub>2</sub>C<sub>2</sub>S<sub>4</sub> center in **1**·Cl<sub>2</sub> does not suffer degradation by Cl<sub>2</sub>; however, under more aggressive conditions,

- (14)  $(\text{Cp}^*\text{Rh})_2(\text{C}_2\text{S}_4)$  (**1**). To a stirred slurry of 0.18 g (0.26 mmol) of  $(\text{Cp}^*\text{RhCl})_2(\text{C}_2\text{S}_4)$  in 30 mL of THF under an Ar atmosphere was added 0.60 mL of a 1.0 M solution (0.60 mmol) of LiBHET<sub>3</sub> in THF. After ~1 min, the slurry turned from dark green to dark blue. Solvent was removed under reduced pressure to ~5 mL after 7.5 h. Addition of 50 mL of hexane was followed by filtration. The dark blue solid was washed with 5 × 10 mL of MeOH and 10 mL of Et<sub>2</sub>O and was dried in vacuo. Yield: 88 mg (55%). Anal. Calcd (found) for C<sub>22</sub>H<sub>30</sub>S<sub>4</sub>Rh<sub>2</sub>: C, 42.04 (41.85); H, 4.81 (4.85). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 1.95 (Me<sub>5</sub>C<sub>5</sub>). <sup>13</sup>C NMR (150 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 10.79 (Me<sub>5</sub>C<sub>5</sub>), 97.37 (Me<sub>5</sub>C<sub>5</sub>, J<sub>Rh-C</sub> 6.9 Hz), 169.45 (C<sub>2</sub>S<sub>4</sub>). UV–vis (CH<sub>2</sub>Cl<sub>2</sub>): 688 nm.
- (15) Garcia, J. J.; Torrens, H.; Adams, H.; Bailey, N. A.; Shacklady, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1993**, 1529–1536.
- (16) Dobbs, D. A.; Bergman, R. G. *Inorg. Chem.* **1994**, *33*, 5329–5336.



**Figure 1.** Structure of the non-hydrogen atoms in  $(C_5Me_4Et)_2Rh_2Cl_2(\mu-C_2S_4)$  ( $\mathbf{1}\cdot Cl_2$ ) with thermal ellipsoids set at the 50% probability level. The molecule rests on a crystallographic inversion center. Important bond lengths and angles are Rh(1)–Cl(1), 2.403 Å; Rh(1)–S(1), 2.317 Å; Rh(1)–S(2), 2.334 Å; and Cl(1)–Rh(1)–S(2), 90.1°.



**Figure 2.** Structure of the non-hydrogen atoms in  $Cp^*_2Rh_2(\mu-C_2S_4)$  ( $\mathbf{1}$ ) with thermal ellipsoids set at the 50% probability level. The molecule rests on a crystallographic inversion center. Important bond lengths are Rh(1)–S(1), 2.2432 Å, and Rh(1)–S(2), 2.2517 Å.

excess  $Cl_2$  strips the  $C_2S_4$  ligand from the bimetallic unit to afford  $[Cp^*RhCl_2]_2$ . The two-electron nature of the chlorine addition prompted a search for the half-oxidized species  $Cp^*_2Rh_2Cl(\mu-C_2S_4)$ . Treatment of  $\mathbf{1}$  with  $\sim 0.5$  equiv of  $Cl_2$  consumed 0.5 equiv

of  $\mathbf{1}$ . However, the yield of  $\mathbf{1}\cdot Cl_2$  was low, and we were unable to identify the components of the resulting mixture of  $Cp^*$ -containing products.

The complexities associated with the partial chlorination of  $\mathbf{1}$  can be understood, in part at least, in the context of the electrochemical properties of  $\mathbf{1}$ . The cyclic voltammetry of  $\mathbf{1}$  is unexceptional in the anodic direction, showing a reversible reduction process at  $-1.36$  V (vs Ag/AgCl), corresponding to the formation of  $\mathbf{1}^-$ . More interesting, the oxidation of  $\mathbf{1}$  at 0.385 V triggers a coupled electrochemical–chemical sequence (EC process). Thus, oxidation of  $\mathbf{1}$  is irreversible because the resulting cation  $\mathbf{1}^+$  is associated with a chemical process that we propose is the dimerization of  $\mathbf{1}^+$ .<sup>17</sup> The corresponding reduction of  $[\mathbf{1}^+]_2$  occurs at  $-0.44$  V; it is clear from the CV that this reduction regenerates  $\mathbf{1}$ .

In summary, we have for the first time elucidated the structural chemistry of a  $M_2C_2S_4$  core in two oxidation states. The rich redox properties of the  $M_2C_2S_4$  core encourage the further development of reaction centers based on the  $M_2C_2S_4$  core. The electrochemical results indicate that this  $C_2S_4^{4-}$  complex is susceptible to condensation processes, implicating novel bonding modes for  $C_2S_4$ .

**Acknowledgment.** This research was funded by the Department of Energy (DEFG02-96ER45439). G.A.H. is supported by a graduate fellowship from the Fannie and John Hertz Foundation.

**Supporting Information Available:** Crystallographic information and tables of atomic parameters, bond lengths, and bond angles for  $\mathbf{1}\cdot Cl_2$  and  $\mathbf{1}$ ; also, CV of  $\mathbf{1}$  showing EC process. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC990150E

(17) Oxidation of  $\mathbf{1}$  with 1 equiv of  $[CpFe(C_5H_4C(O)CH_3)]BF_4$  followed by anion metathesis with  $NaBPh_4$  (in MeOH solution) afforded  $[\mathbf{1}^+]_2(BPh_4)_2$ . The  $^1H$  NMR spectrum of  $[\mathbf{1}^+]_2(BPh_4)_2$  confirms its empirical formula, high symmetry (one  $Cp^*$  signal), and diamagnetism.