

## Carbon Sulfide Bridging Ligands: Synthesis of New Electroactive Ensembles

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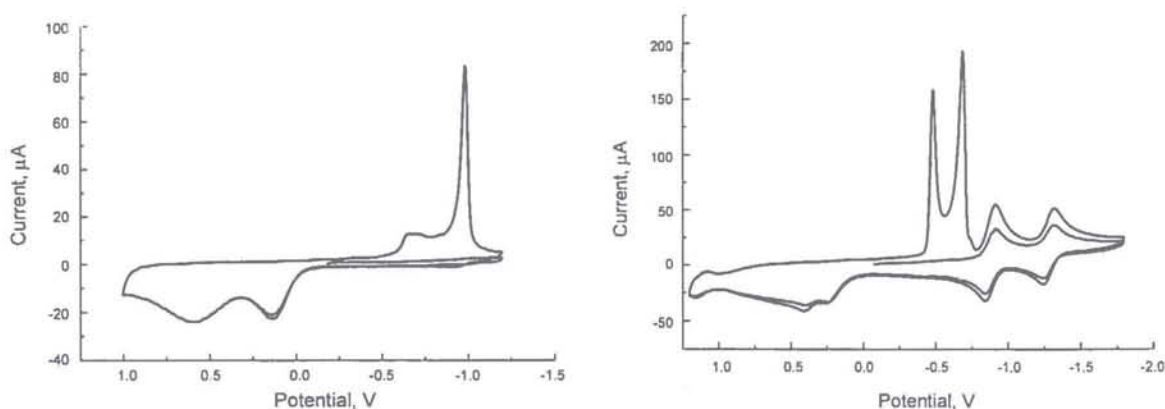
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Dithiolenes are important electroactive ligands. The non-innocent redox nature of metal dithiolene complexes facilitates numerous applications. Some recent applications of metal dithiolenes include modeling Mo- and W-containing enzyme active sites,<sup>1,2</sup> preparing conductive materials,<sup>3</sup> and separating olefins electrochemically.<sup>4</sup>

The thiooxalates, specifically tetrathiooxalate (TTO)  $C_2S_4^{2-}$ , are closely related to the dithiolenes. Early attempts to prepare  $C_2S_4^{2-}$  from sodium reduction of  $CS_2$  resulted in the discovery of  $C_3S_5^{2-}$ , a dithiolene of much interest.<sup>5</sup> The successful synthesis of TTO was accomplished by an electrochemical route and a chemical route.<sup>6,7</sup> Unfortunately, the former requires specialized equipment, and the latter is a low yield reaction of  $C_2Cl_4$  with  $Na_2S_2$ . A related dianion  $C_4S_6^{2-}$  can be synthesized by several low yield reactions that proceed through a  $C_2S_4$  intermediate.<sup>7,8</sup> Semi-conducting oligomers of the formula  $[M(C_2S_4)]_n$  ( $M = Ni, Cu, Pd, Pt$ ) and  $[Ni(C_4S_6)]_n$  have been investigated.<sup>8,9</sup>

Our work has focused on improving the synthesis of  $C_2S_4^{2-}$  and of  $C_4S_6^{2-}$ . The complex apparatus for electrochemical synthesis of TTO can be simplified so that basic laboratory equipment can be used. The synthesis and purification of  $C_4S_6^{2-}$  is best accomplished by the oxidation of TTO with  $I_2$  in two steps: the first step allows for the side product  $NEt_4I$  to be washed away and makes purification possible. The electrochemical properties of  $(NEt_4)_2C_2S_4$  (left) and of  $(NEt_4)_2C_4S_6$  (right) were probed by cyclic voltammetry (CV) (Figure 1). The results indicate that TTO undergoes dimerization upon one-electron oxidation and that  $C_4S_6^{2-}$  can be reduced to a 3- radical ion as well as a 4- ion.



**Figure 1**

Although TTO cannot be reduced to the tetranion in solution, there are numerous examples of metal complexes formally containing  $C_2S_4^{4-}$  (e.g.  $Cp^*Ni_2(C_2S_4)$ ),

$\text{Cp}_4\text{Ti}_2(\text{C}_2\text{S}_4)$ , and  $[(\text{triphos})_2\text{Rh}_2(\text{C}_2\text{S}_4)]^{2+}$ .<sup>10-12</sup> The C-C distance is used as the structural criterion to determine the oxidation state, i.e. 1.46 Å for  $\text{C}_2\text{S}_4^{2-}$  and 1.36 Å for  $\text{C}_2\text{S}_4^{4-}$ .<sup>10,13</sup> We have developed the first system in which both oxidation states of  $\text{C}_2\text{S}_4$  can be isolated and structurally characterized. Interconversion of  $\text{Cp}^*_2\text{M}_2\text{Cl}_2(\text{m}-\text{C}_2\text{S}_4)$  and  $\text{Cp}^*_2\text{M}_2(\text{m}-\text{C}_2\text{S}_4)$  occurs according to the scheme shown in Figure 2 ( $\text{M} = \text{Rh}, \text{Ir}$ ).<sup>14</sup> The analogous  $\text{Cp}^*_2\text{Rh}_2\text{Cl}_2(\text{m}-\text{C}_4\text{S}_6)$  complex cannot be reduced to a  $\text{C}_4\text{S}_6^{4-}$  complex. Reactions of  $(\text{NEt}_4)_2\text{C}_2\text{S}_4$  and  $(\text{NEt}_4)_2\text{C}_4\text{S}_6$  with  $\text{W}(\text{S}_2\text{C}_2\text{Ph}_2)_4(\text{CO})_2$  demonstrate that  $\text{C}_4\text{S}_6$  can be degraded into  $\text{C}_2\text{S}_4$ .

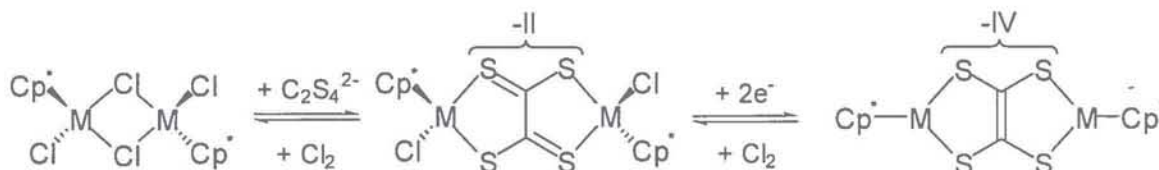


Figure 2

The bonding modes of  $\text{C}_2\text{S}_4$  in metal complexes are rather limited. The ligand always bridges homometallic fragments and exclusively forms 5-member rings by binding metals in a 1,2-dithiolene fashion, except in the case of  $\text{Fe}_4(\text{CO})_{12}(\text{C}_2\text{S}_4)$ .<sup>15,16</sup> Using  $\text{Cp}^*_2\text{Rh}_2(\text{m}-\text{C}_2\text{S}_4)$  as a building block, we have been able to synthesize multimetallic ensembles that possess three new bonding modes for  $\text{C}_2\text{S}_4$ .<sup>17</sup> The CV of  $\text{Cp}^*_2\text{Rh}_2(\text{m}-\text{C}_2\text{S}_4)$  shows that the complex undergoes electrochemically induced reversible aggregation (Figure 3). Synthesis and isolation of the new tetrarhodium complex  $[\text{Cp}^*_4\text{Rh}_4(\text{C}_2\text{S}_4)_2]\text{X}_2$  ( $\text{X} = \text{BF}_4^-, \text{BPh}_4^-$ ) followed. We investigated the synthesis of two other multimetallic ensembles based upon the reaction of  $\text{Cp}^*_2\text{Rh}_2(\text{m}-\text{C}_2\text{S}_4)$  with cationic  $\text{Cp}^*\text{M}$  fragments,  $(\text{Cp}^*\text{Ru})^+$  and  $(\text{Cp}^*\text{Rh})^{2+}$ . The  $\text{Cp}^*\text{Ru}$  reaction forms a trimetallic product with a Rh-Ru bond whereas the  $\text{Cp}^*\text{Rh}$  reaction forms a hexarhodium complex with no Rh-Rh bond. These three new bonding modes set a precedent for possible bonding within conductive materials based upon complexes of  $\text{C}_2\text{S}_4$ .

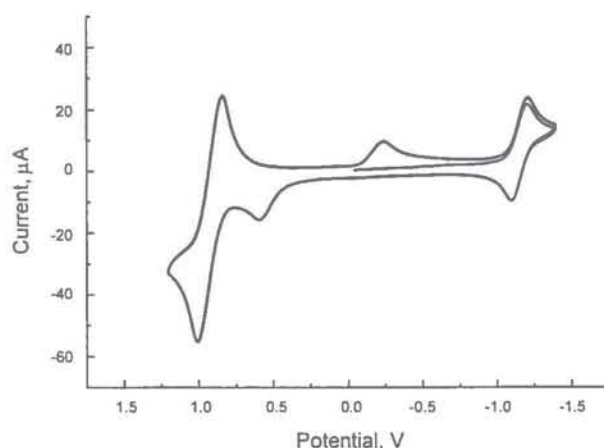


Figure 3

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