

buten-3-yne,<sup>11</sup> not 1,4-diphenyl-1-buten-3-yne. The assignment of the stereochemistry of **4** was made on the basis of its <sup>1</sup>H NMR spectra.<sup>12</sup> Solvents like toluene, CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub>, or THF were less efficient (data not shown) than dioxane. When the reaction was conducted by using Me<sub>3</sub>SiBr or Me<sub>3</sub>SiOTf instead of **1**, no reaction took place. The reaction with propynyltributylstannane (**3b**) gave 1-silyl-1-penten-3-yne with high stereoselectivity (entries 2, 4, and 5-7). Use of [(trimethylsilyl)ethyl]tributylstannane (**3c**) led to a slightly lower stereoselectivity (entry 3).<sup>13</sup> It is noteworthy that the bromine atom in **2e** remained intact under the reaction conditions (entry 7), although Pd-catalyzed coupling reaction of bromobenzene with organostannanes is well-known.<sup>14</sup> The reaction using Me<sub>3</sub>SiMe<sub>2</sub>I in place of **1** gave (*Z*)-2-phenyl-1-[(trimethylsilyl)dimethylsilyl]-1-penten-3-yne (**11**) (entry 8) without the cleavage of the Si-Si bond.<sup>4,6b</sup> Although other organostannanes such as allyl- and vinylstannane were also applicable to the present coupling reaction, the stereoselectivity was low (entries 9 and 10). The decrease in stereoselectivity<sup>13</sup> may reflect the relative rates of transmetalation (organic group transfer) for organostannanes, as has been observed by Stille.<sup>14a</sup>

The proposed reaction mechanism is shown in Scheme I. A first step of the catalytic cycle would be the oxidative addition of **1** to the palladium(0) catalyst to give a silylpalladium iodide **14**. Silylpalladation<sup>15</sup> of an acetylene with **14** yields vinylpalladium species **15**. The transmetalation of an organostannane followed by reductive elimination gives the coupled product,<sup>14</sup> regenerating the palladium(0) catalyst. Silylpalladation of acetylene with **14** would be the regio- and stereodetermining step, since it is established that the succeeding step of reductive elimination proceeds with a retention of configuration.<sup>14</sup> The results shown in entries 7 and 8 suggest that oxidative addition of the Si-I bond in **1** predominated, interestingly, over that of C-Br and Si-Si under the present reaction conditions.

These results suggest new possibilities of designing various catalytic reactions on the basis of oxidative addition of halosilanes and of silylmatalation. The present reaction offers a new synthetic method for stereodefined conjugated enynes, which are important in the synthesis of a wide range of natural products and other complex organic molecules.<sup>16</sup> A search for other coupling reactions along these lines is in progress.

**Acknowledgment.** This work is supported in part by grants from the Ministry of Education, Science, and Culture, Japan. We thank the Analytical Center, Faculty of Engineering, Osaka University, for the use of JEOL and Bruker NMR spectrometers.

**Supplementary Material Available:** Spectral data and elemental analyses for the products (5 pages). Ordering information is given on any current masthead page.

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## Preparation of the Thiosulfonato Complexes CpRu(PPh<sub>3</sub>)(CO)SS(O)R, Where R = C<sub>3</sub>H<sub>7</sub>, CHMe<sub>2</sub>, and 4-C<sub>6</sub>H<sub>4</sub>Me, and the Structure for R = CHMe<sub>2</sub>. Oxygen Transfer To Give the Thiosulfonato Complex CpRu(PPh<sub>3</sub>)(CO)SS(O)<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>Me and Its Structure

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Transition-metal complexes containing thiosulfonato ligands, RS(O)S<sup>-</sup>, are practically unknown. They have been the subject of speculation<sup>1</sup> as possible precursors to organic thiosulfinate esters, which have a broad spectrum of biological activity.<sup>2</sup> The complexes CpW(CO)<sub>3</sub>SS(O)R have been prepared,<sup>3</sup> but they were unstable, and no X-ray structure was reported.<sup>4</sup> Transition-metal thiosulfonato complexes are also unknown.<sup>5</sup> They would contain the MSS(O)<sub>2</sub>R moiety and, thus, would be homologues of the well-known metal sulfonates MS(O)<sub>2</sub>R.<sup>6</sup> The coordinating ability of small sulfur oxide ligands is well documented<sup>1,7</sup> and of interest with respect to SO<sub>2</sub>-pollution abatement.<sup>8</sup> We have prepared a number of complexes containing rare polysulfano ligands of the type RS<sub>x</sub><sup>-</sup>, where *x* = 2, 3.<sup>9</sup> Therefore, oxidized ligands of the type RS<sub>x</sub>(O)<sub>y</sub><sup>-</sup> became natural targets of preparative studies. We report the rational synthesis of ruthenium thiosulfonato complexes and an unexpected conversion via a novel oxygen transfer to give a ruthenium thiosulfonato complex.

The preparation of organic thiosulfinate esters (RSS(O)R') via oxidation of the disulfides is not practical.<sup>5d</sup> Unsymmetrical esters can readily be prepared via reaction of a thiol with a sulfinyl transfer reagent of the type RS(O)(phth), where phth = phthalimido.<sup>10</sup> Similarly, oxidation of the tungsten disulfano moiety in CpW(CO)<sub>3</sub>SSR gave a complex mixture of several products.<sup>3</sup> However, treatment of the metal thiol CpRu-(PPh<sub>3</sub>)(CO)SH<sup>11</sup> with RS(O)(phth) in THF, under N<sub>2</sub>, at room

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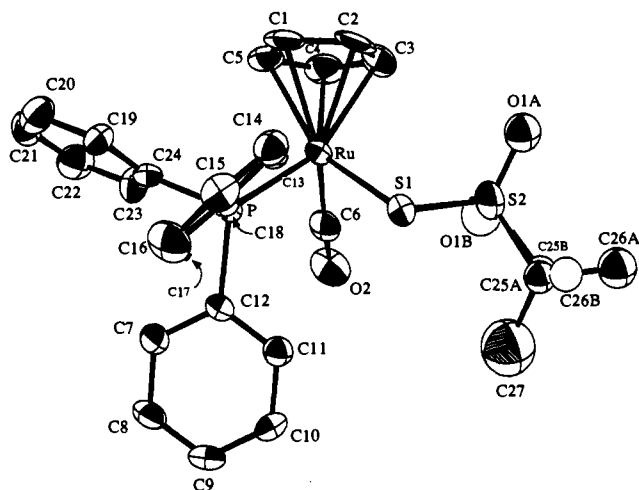
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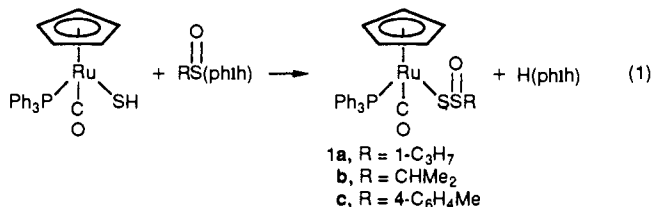
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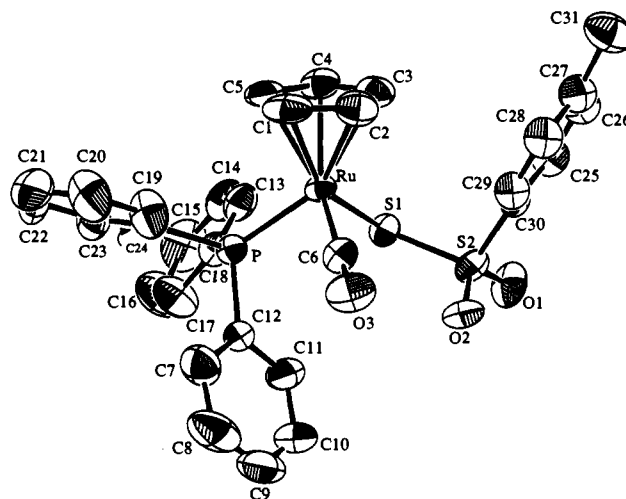
**Figure 1.** ORTEP drawing of  $\text{CpRu}(\text{PPh}_3)(\text{CO})\text{SS}(\text{O})\text{CHMe}_2$  (**1b**): Ru-S1, 2.379 (2); S1-S2, 2.076 (3); S2-O1A, 1.45 (1); S2-C25A, 1.97 (2); Ru-S1-S2, 102.6 (1); S1-S2-O1A, 110.1 (4); S1-S2-C25A, 91.5 (4); Ru-S1-S2-C25A, 70.4. Atoms labeled "A" are 60% occupancy; atoms labeled "B" are 40% occupancy.

temperature gave, after chromatography on alumina, the air-stable yellow complexes  $\text{CpRu}(\text{PPh}_3)(\text{CO})\text{SS}(\text{O})\text{R}$ , eq 1.<sup>12</sup>



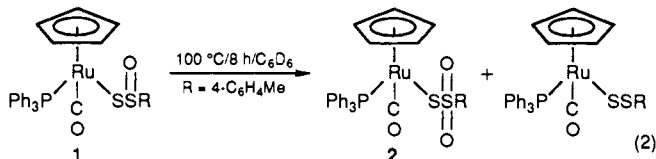
The NMR spectra of these complexes<sup>12c</sup> are consistent with the presence of diastereomers due to the chiral sites at the ruthenium atom and at the oxidized sulfur atom. The diastereomers for **1c** were partially separated via fractional crystallization. NMR spectra of enriched samples in C<sub>6</sub>D<sub>6</sub> in sealed NMR tubes at 100 °C were unchanged with respect to the peak shapes or their relative intensities as observed at room temperature. This suggests that both chiral centers are configurationally stable. The thermal and configurational stability of **1a-c** is noteworthy since simple alkyl thiosulfinate esters are described as being unstable.<sup>5,13,14</sup>

The crystal structure of **1b**, shown in Figure 1,<sup>15</sup> confirms the presence of the alkylthiosulfinate ligand as expected from the logic of the synthesis. The sulfinyl oxygen atom is disordered in a manner consistent with the presence of epimers about the chiral sulfinyl sulfur atom. The occupancies of the two positions refined to give a ratio of 3:2, exactly the same as observed for the diastereomers in the NMR spectrum. The bond lengths and angles in the novel RuSS(O)CHMe<sub>2</sub> moiety are within the ranges observed for complexes of the type  $\text{CpRu}(\text{PPh}_3)(\text{CO})\text{S}_x\text{R}$ , where  $x = 1-3$ ,<sup>16</sup> and for organic thiosulfinate esters.<sup>17</sup>



**Figure 2.** ORTEP drawing of  $\text{CpRu}(\text{PPh}_3)(\text{CO})\text{SS}(\text{O})_2\text{-4-C}_6\text{H}_4\text{Me}$  (**2**): Ru-S1, 2.383 (2); S1-S2, 2.023 (3); S2-O1, 1.444 (8); S2-O2, 1.435 (6); S2-C30, 1.770 (8); Ru-S1-S2, 110.0 (1); S1-S2-O1, 105.7 (2); S1-S2-O2, 113.0 (3); S1-S2-C30, 107.0 (3); O1-S2-O2, 117.4 (3); O1-S1-C30, 106.9 (3); O2-S2-C30, 106.3 (4); Ru-S1-S2-C30, 41.1.

Although heating **1c** for brief periods as described above did not interconvert its diastereomers, prolonged heating of a sample led to the gradual appearance in the NMR spectrum of peaks due to three Cp-ruthenium species at the expense of the starting complex (eq 2). Two of the three complexes were identified by



comparison of their peak positions to those of authentic samples of the thiolato complex  $\text{CpRu}(\text{PPh}_3)(\text{CO})\text{S-4-C}_6\text{H}_4\text{Me}^{11b}$  and the disulfano complex  $\text{CpRu}(\text{PPh}_3)(\text{CO})\text{SS-4-C}_6\text{H}_4\text{Me}^{16}$ . X-ray crystallographic analysis identified the third<sup>12c</sup> as the novel ruthenium thiosulfonato complex  $\text{CpRu}(\text{PPh}_3)(\text{CO})\text{SS}(\text{O})_2\text{-4-C}_6\text{H}_4\text{Me}$  (**2**) (Figure 2<sup>18</sup>). To our knowledge, this is the first metal thiosulfonato complex to be reported. The general features of the structure of **2** are very similar to those of **1b** and of the disulfano complex  $\text{CpRu}(\text{PPh}_3)(\text{CO})\text{SSCHMe}_2$ .<sup>16</sup> The sulfur-sulfur distance in **2** is slightly shorter than that in **1b**, but the ruthenium-sulfur distances are very similar in both complexes. The presence of the additional oxygen atom in the sulfur ligand of **2** shifts the carbonyl stretching frequency to slightly higher wavenumbers, as might be expected.<sup>12d</sup> The bond lengths and angles of the RuSS(O)<sub>2</sub>R moiety are within the ranges expected.<sup>16,19</sup>

The stoichiometry of eq 2 assumes the source of the thiolato complex observed in the NMR spectrum to be desulfurization of the disulfano complex.<sup>16</sup> Consistent with this, the relative integrated intensities of the Cp peaks of the three species gave their relative concentrations as **2** (1), disulfano (0.65), and thiolato (0.35). Thus, **2** seemingly results via oxygen atom disproportionation.

(12) (a) Yield: **1a**, 48%; **1b**, 33%; **1c**, 41%. (b) Satisfactory elemental analyses were obtained for **1a-c**. (c) The preparative procedures and the NMR data for **1a-c** and **2** are given in the supplementary material.

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(15) Crystal data for **1b**: C<sub>27</sub>H<sub>27</sub>O<sub>2</sub>PS<sub>2</sub>Ru; space group P1̄, λ(Cu Kα), a = 10.490 (2) Å, b = 14.663 (4) Å, c = 8.606 (4) Å, α = 97.85 (3)°, β = 105.21 (2)°, γ = 82.94 (2)°, V = 1260.1 (7) Å<sup>3</sup>, Z = 2, D<sub>calc</sub> = 1.509 g cm<sup>-3</sup>, R = 0.053, R<sub>w</sub> = 0.073 (I > 3σ(I)) for 3092 (82%) reflections where I > 3σ(I). The crystal structure was solved by Dr. James Britten, Manager, Single-Crystal Crystallographic Facility, Department of Chemistry, McGill University, using data collected by the Molecular Structure Corporation, Houston, TX, at -120.0 °C. The full structural report is included in the supplementary material.

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tionation of **1c**. This resembles the disproportionation of an  $\text{SO}_2$  adduct of  $\text{Cp}^*_2\text{Mo}_2(\mu\text{-S}_2)(\mu\text{-S})_2$  to give an  $\text{SO}_3$  adduct and  $\text{S}_8$ , the latter via  $\text{SO}_7^{\text{th}}$ . Such reactions are a feature of organic thiosulfinate ester chemistry;<sup>2b,13a,b</sup> however, the conditions required for **1c** to react are much more extreme than those required for organic systems. The initiating step in the complex decomposition process of the latter<sup>2b,13b,20</sup> is loss of a proton from the alkyl group attached to the sulfonyl sulfur (i.e.,  $\beta$ -elimination<sup>2b</sup>). In **1a-c** this position is occupied by the ruthenium atom. Organic thiosulfinate esters are also readily deoxygenated by triphenylphosphine,<sup>17b</sup> but **1** did not react. Oxygen transfer has been postulated<sup>21</sup> to explain the apparent difficulty in stopping the oxidation of thiolato complexes at the sulfoxide stage ( $\text{MS}(\text{O})\text{R}$ ), sulfones ( $\text{MS}(\text{O})_2\text{R}$ ) being invariably obtained.<sup>21-23</sup>

The catenated polysulfur oxide ligands of **1a-c** and **2** juxtapose reduced and oxidized sulfur atoms and thus are of interest with respect to the Claus reaction, wherein  $\text{H}_2\text{S}$  and  $\text{SO}_2$  combine to give sulfur and water, the mechanism of which is poorly understood.<sup>24</sup>

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**Supplementary Material Available:** Experimental procedures for the preparation of **1a-c** and **2**, tables of NMR data for **1a-c** and **2** and crystal data, atomic coordinates, thermal parameters, and bond lengths for angles for **1b** and **2** (25 pages); tables of final observed and calculated structure factors for **1b** and **2** (42 pages). Ordering information is given on any current masthead page.

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## The First Stable Enethiolizable Thioaldehyde via a Zirconocene $\eta^2$ -Thioacyl Complex

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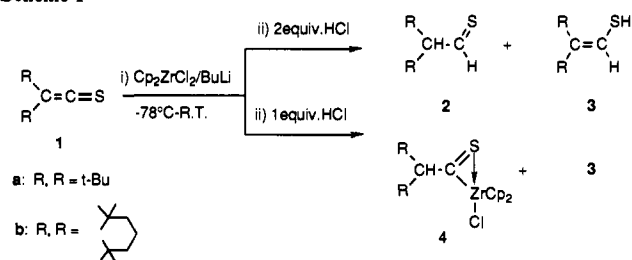
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The group 4 metallocenes, i.e.,  $\text{Cp}_2\text{M}$  ( $\text{M} = \text{Ti}, \text{Zr}$ ),<sup>1a,b</sup> and their equivalents<sup>1c-h</sup> are well-known to exhibit high reactivity such as carbenoid like behavior and to add to a variety of unsaturated compounds to give  $\text{Cp}_2\text{M}$  complexes.<sup>2,3</sup> The high degree of

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## Scheme I



$\pi$ -back-bonding from the metal to the organic fragment makes the resulting complex behave more like metallacyclopropane,<sup>3c</sup> metallacyclopropene,<sup>1c,3a-c</sup> metallaioxirane,<sup>3e-1</sup> and metallathirane,<sup>1e,3d</sup> respectively. These unique aspects of group 4 metallocenes have their parallels in the main-group chemistry of carbene and bivalent group 14 metals, e.g., the reactivity of silylene<sup>4a-d</sup> and germylene<sup>4e,f</sup> toward ketones, thio ketones, and heterocumulenes. Summarizing our initial attempts in this area, we describe that the addition reactions of zirconocene to thio ketenes (**1**) followed by acidolysis offer a novel route to stable thioaldehydes (**2**)<sup>5</sup> and their enethiol isomers (**3**) as well as  $\eta^2$ -thioacyl complexes of zirconium (**4**).<sup>6</sup> These represent not only the first enethiolizable thioaldehyde but also the first structurally characterized thioacyl complex of an early transition metal.<sup>6d</sup>

To a tetrahydrofuran (THF) solution of a " $\text{Cp}_2\text{Zr}$ " equivalent [ $\text{Cp}_2\text{Zr}(n\text{-Bu})_2$ ] (1.1 mmol) prepared from  $\text{Cp}_2\text{ZrCl}_2$  and  $\text{BuLi}$ <sup>1f,g</sup> was added a solution of thio ketene (**1a** or **1b**) (1.1 mmol) in THF at  $-78^\circ\text{C}$ . The reaction mixture changed from purple to orange

(2) Several synthetic methods for preparing  $\text{Cp}_2\text{M}$  complexes ( $\text{M} = \text{Ti}, \text{Zr}$ ) have been reported. Among those, direct combination of a " $\text{Cp}_2\text{M}$ " equivalent and an unsaturated organic fragment is limited to isolation of alkene,<sup>1c,f-h</sup>  $\eta^2(\text{C},\text{O})$ -ketene,<sup>1d</sup> and thio ketene complexes.<sup>1e</sup> Recently the concerted methane and benzene elimination of methyl and phenylalkyl-zirconocene derivatives was utilized to prepare complexes of cycloalkenes,<sup>3c</sup> arynes,<sup>3a-c</sup> and  $\eta^2$ -thioaldehyde.<sup>3d</sup>  $\eta^2$ -Ketone and aldehyde complexes are generally prepared by migration of metal alkyl or hydride to a *cis*-acyl ligand.<sup>3e-i</sup> The deprotonation of an  $\alpha$ -proton of an acyl complex affords an efficient route to  $\eta^2(\text{C},\text{O})$ -ketene complexes.<sup>3j-1</sup>

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