

# Half-Sandwich Ruthenium Phosphine Complexes with Sulfur-Donor Ligands. X-ray Crystal Structures of $[\text{Cp}^*\text{RuH}(\text{SH})(\text{PEt}_3)_2][\text{BPh}_4]$ and $[\text{Cp}^*\text{Ru}(\text{S}_2\text{CO}^i\text{Pr})(\text{PEt}_3)]$

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The complexes  $[\text{CpRuCl}(\text{PEt}_3)_2]$  (**1**) and  $[\text{CpRuCl}(\text{PMe}^i\text{Pr}_2)(\text{PPh}_3)]$  (**2**) react with  $\text{H}_2\text{S}$  in EtOH in the presence of  $\text{NaBPh}_4$  furnishing the green persulfide derivatives  $\{[\text{CpRu}(\text{L})]_2(\mu\text{-S}_2)[\text{BPh}_4]_2$  ( $\text{L} = (\text{PEt}_3)_2, (\text{PMe}^i\text{Pr}_2)(\text{PPh}_3)$ ), which were also obtained by reaction of **1** or **2** with elemental sulfur and  $\text{NaBPh}_4$  in MeOH. At variance with this, the reaction of  $[\text{Cp}^*\text{RuCl}(\text{PEt}_3)_2]$  (**3**) with  $\text{H}_2\text{S}$  in EtOH afforded the  $\text{Ru}^{\text{IV}}$  hydrido-metallothiol  $[\text{Cp}^*\text{RuH}(\text{SH})(\text{PEt}_3)_2][\text{BPh}_4]$ , which has been structurally characterized, derived from the oxidative addition of  $\text{SH}_2$  to the electron-rich  $\text{Ru}^{\text{II}}$  moiety  $\{[\text{Cp}^*\text{Ru}(\text{PEt}_3)_2]^+\}$ . This compound is oxidized to yield the persulfide complex  $\{[\text{Cp}^*\text{Ru}(\text{PEt}_3)_2]_2(\mu\text{-S}_2)[\text{BPh}_4]_2$ , which was also obtained by reaction of **3** with elemental sulfur. The reaction of **1**, **2**, and **3** with 2-mercapto-pyridine (HSPy) in EtOH yielded cationic complexes in which HSPy is tautomerized to its 1*H*-pyridine-thione form as inferred from spectral data. Compound **1** reacts with potassium alkyl-xanthates  $\text{KS}_2\text{COR}$  ( $\text{R} = \text{Me}, \text{Et}, ^i\text{Pr}$ ) yielding compounds of the type  $[\text{CpRu}(\eta^1\text{-S}_2\text{COR})(\text{PEt}_3)_2]$ , whereas the reaction of **2** and **3** led respectively to the complexes  $[\text{CpRu}(\eta^2\text{-S}_2\text{COR})(\text{PMe}^i\text{Pr}_2)]$  and  $[\text{Cp}^*\text{Ru}(\eta^2\text{-S}_2\text{COR})(\text{PEt}_3)]$ , which contain one bidentate xanthate and one phosphine. The X-ray crystal structure of  $[\text{Cp}^*\text{Ru}(\text{S}_2\text{CO}^i\text{Pr})(\text{PEt}_3)]$  was determined. In analogous fashion, the reaction of **1** with sodium diethyldithiocarbamate yielded  $[\text{CpRu}(\eta^1\text{-S}_2\text{CNET}_2)(\text{PEt}_3)_2]$ , whereas **2** and **3** afforded the corresponding derivatives  $[\text{CpRu}(\eta^2\text{-S}_2\text{CNET}_2)(\text{PMe}^i\text{Pr}_2)]$  and  $[\text{Cp}^*\text{Ru}(\eta^2\text{-S}_2\text{CNET}_2)(\text{PEt}_3)]$ .

## Introduction

There has been increasing interest in the chemistry of transition metal complexes with sulfur-containing ligands<sup>1</sup> because they provide model compounds for biologically redox-active metalloproteins<sup>2</sup> and other systems involved in processes such as nitrogen fixation.<sup>3</sup> If  $\text{H}_2\text{S}$  is considered, the interest arises not only because of its relevance to the biological sulfur cycle but also for its implication in the formation of ores and in hydrodesulfurization catalysis, as well as the potential use of  $\text{H}_2\text{S}$  as a source of  $\text{H}_2$  and organosulfur compounds.<sup>4–9</sup> However, there are very few examples of

complexes containing coordinated  $\text{H}_2\text{S}$ .<sup>4,10–13</sup> Those reported are in general rather unstable and very reactive, and only in recent years have  $\text{H}_2\text{S}$  complexes been unequivocally characterized by X-ray crystallography.<sup>12,13</sup> The first structure was reported by Sellmann and co-workers for the  $\text{Ru}^{\text{II}}$  complex  $[\text{Ru}(\text{S}_4)(\text{PPh}_3)(\text{SH}_2)]\cdot\text{THF}$  ( $\text{S}_4 = 1,2\text{-bis}[(2\text{-mercaptophenol})\text{thio}]\text{-ethane}$ ), the crystal stability resulting from intermolecular H-bonding involving the THF solvate and strong  $\text{S}\cdots\text{H}$  bridging.<sup>12</sup> More recently, the crystal structure of the adduct  $[\text{RuCl}_2(\text{P}-\text{N})(\text{PTol}_3)(\text{SH}_2)]\cdot 0.5\text{ THF}\cdot 0.41\text{H}_2\text{O}$  ( $\text{P}-\text{N} = o\text{-}(\text{diphenylphosphino})\text{-}N,N\text{-dimethylaniline}$ ) has been reported, this being the first example of a structurally characterized transition metal– $\text{H}_2\text{S}$  complex formed under ambient conditions.<sup>4,13</sup> This sort of complexes easily undergoes a variety of chemical transformations which generally lead to oligomeric sulfur-bridged species.<sup>10,12</sup> At variance with this, oxidative addition of  $\text{H}_2\text{S}$  at a metal center to yield hydrido-

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metallothiol species seems to be a more common reactivity pattern.<sup>4,5,8,14,15</sup> It has been observed in reactions with hydrides and other electron-rich metal complexes, although very often the hydrido-metallothiol reacts further with H<sub>2</sub>S, yielding bis(mercapto) complexes. Thus, the reactions of both [Ru(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] and [Ru(H)<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] with H<sub>2</sub>S at room temperature afforded [RuH(SH)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] and [Ru(SH)<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] sequentially.<sup>5</sup> In analogous fashion, the reaction of [Ru(H)<sub>2</sub>(dppm)<sub>2</sub>] (dppm = 1,2-bis(diphenylphosphino)methane) with H<sub>2</sub>S yielded [RuH(SH)(dppm)<sub>2</sub>], which converts to a mixture of *cis*- and *trans*-[Ru(SH)<sub>2</sub>(dppm)<sub>2</sub>] upon heating or prolonged stirring under H<sub>2</sub>S,<sup>5</sup> whereas [RuH(SH)(PPh<sub>3</sub>)<sub>3</sub>] has been obtained starting from [Ru(H)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] or [Ru(H)<sub>2</sub>(H<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub>] and H<sub>2</sub>S.<sup>14</sup> Amara-sekara and Rauchfuss have suggested the possibility of an equilibrium between the unstable H<sub>2</sub>S complex [CpRu(SH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and its hydrido-metallothiol tautomer [CpRuH(SH)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, but no experimental evidence supporting the existence of the Ru<sup>IV</sup> hydrido-metallothiol was found.<sup>10</sup> Other Ru<sup>II</sup> hydrido-metallothiol derivatives have been prepared by metathetical exchange of NaSH with chloro-hydride complexes, i.e., coordinatively unsaturated [RuH(SH)(CO)(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>].<sup>16</sup>

As a part of our studies on the chemistry of half-sandwich ruthenium complexes with sulfur-containing ligands, we have now considered their reactivity toward H<sub>2</sub>S. No H<sub>2</sub>S adducts were isolated or detected, and instead, binuclear persulfido complexes were obtained. However, in the course of the reaction of H<sub>2</sub>S with the electron-rich complex [Cp<sup>\*</sup>RuCl(PEt<sub>3</sub>)<sub>2</sub>] the unprecedented Ru<sup>IV</sup> hydrido-metallothiol [Cp<sup>\*</sup>RuH(SH)(PEt<sub>3</sub>)<sub>2</sub>]-[BPh<sub>4</sub>] was obtained, and its structure has been determined by X-ray crystallography. We have also prepared and characterized a series of ruthenium derivatives with sulfur-donor ligands such as 2-mercapto-pyridine, alkyl-xanthates, and diethylthiocarbamate, in an attempt to establish the possible factors that control their different ways of coordination. From this study, alkyl-xanthates and diethylthiocarbamate might be used as hemilabile ligands in organometallic complexes given their capability for adopting an η<sup>1</sup>- or η<sup>2</sup>-coordination mode depending upon the conditions.<sup>17</sup>

## Experimental Section

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk techniques. THF, Et<sub>2</sub>O, and petroleum ether (boiling point range 40–60 °C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. PEt<sub>3</sub> was purchased from Aldrich, whereas PMe<sup>i</sup>Pr<sub>2</sub> was obtained by reaction of PCl<sup>i</sup>Pr<sub>2</sub> (Aldrich) with MeMgI in Et<sub>2</sub>O. [CpRuCl(PEt<sub>3</sub>)<sub>2</sub>] and [CpRuCl(PMe<sup>i</sup>Pr<sub>2</sub>)(PPh<sub>3</sub>)] were obtained by thermal displacement of PPh<sub>3</sub> from [CpRuCl(PPh<sub>3</sub>)<sub>2</sub>]<sup>18</sup> by the corresponding phosphine. [Cp<sup>\*</sup>RuCl(PEt<sub>3</sub>)<sub>2</sub>] was prepared by Zn reduction of the dimer [(Cp<sup>\*</sup>RuCl<sub>2</sub>)<sub>2</sub>]<sup>19</sup> in THF in the

presence of PEt<sub>3</sub>. IR spectra were recorded in Nujol mulls on a Perkin-Elmer FTIR Spectrum 1000 spectrophotometer. UV–vis measurements were made using a Milton Roy Spectronic 3000 diode array. NMR spectra were taken on Varian Unity 400 MHz or Varian Gemini 200 MHz spectrometers. Chemical shifts are given in ppm from SiMe<sub>4</sub> (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}) or 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P{<sup>1</sup>H}). Microanalyses were performed by the Serveis Científic-Tècnics, Universitat de Barcelona.

**CAUTION:** H<sub>2</sub>S is extremely toxic, and all the preparations involving its use should be carried out in a well-ventilated fume hood!

**[CpRu(PEt<sub>3</sub>)<sub>2</sub>Cl] (1) and [CpRu(PPh<sub>3</sub>)(P<sup>i</sup>Pr<sub>2</sub>Me)Cl] (2).** To a slurry of [CpRuCl(PPh<sub>3</sub>)<sub>2</sub>] (1.97 g, ca. 2.7 mmol) in toluene (15 mL) was added PEt<sub>3</sub> (0.8 mL, ca. 5.4 mmol) or PMe<sup>i</sup>Pr<sub>2</sub> (0.4 mL, ca. 2.7 mmol). The mixture was refluxed for 3 h. Then, the solvent was removed in vacuo. The resulting orange oil was dissolved in each case in the minimum amount of petroleum ether and passed through a silica gel chromatographic column in order to remove PPh<sub>3</sub>. This can be done in the air. The column was eluted with petroleum–Et<sub>2</sub>O (3:1 v/v). The fraction corresponding to the orange band was collected. Removal of the solvent afforded an orange (1) or yellow (2) microcrystalline material. Analytically pure samples were obtained by recrystallization from petroleum–Et<sub>2</sub>O. Yield: 75–80%. **1:** Anal. Calcd for C<sub>17</sub>H<sub>35</sub>ClP<sub>2</sub>Ru: C, 46.6; H, 8.06. Found: C, 46.8; H, 8.02. NMR (C<sub>6</sub>D<sub>6</sub>) δ: (<sup>1</sup>H) 1.08 (m, PCH<sub>2</sub>CH<sub>3</sub>); 1.78 (dm, PCH<sub>2</sub>CH<sub>3</sub>); 4.39 (s, C<sub>5</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H}: 32.7 (s). <sup>13</sup>C{<sup>1</sup>H}: 8.27 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 21.2 (t, J(C,P) = 12.4 Hz, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 76.9 (s, C<sub>5</sub>H<sub>5</sub>). **2:** Anal. Calcd for C<sub>30</sub>H<sub>37</sub>ClP<sub>2</sub>Ru: C, 60.4; H, 6.26. Found: C, 60.4; H, 6.29. NMR (C<sub>6</sub>D<sub>6</sub>) δ: (<sup>1</sup>H) 0.64 (d, PCH<sub>3</sub>); 0.82, 1.00, 1.27 (m, P(CH<sub>3</sub>)<sub>2</sub>); 1.93 (dm, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>); 4.33 (s, C<sub>5</sub>H<sub>5</sub>); 7.05, 7.82 (m, P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H}: 45.0 d, 39.5 d, J(P,P) = 40.9 Hz. <sup>13</sup>C{<sup>1</sup>H}: 3.6 (d, J(C,P) = 20.5 Hz, P(CH<sub>3</sub>(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>)); 18.5, 18.7, 18.9, 19.7 (s, PCH<sub>3</sub>(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>); 32.5 (dd, J(C,P) = 21.2 Hz, P(CH<sub>3</sub>(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>)); 79.8 (s, C<sub>5</sub>H<sub>5</sub>); 129.1, 127.6 (s, P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>), 134.9 (d, J(C,P) = 10.3 Hz, P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>).

**[Cp<sup>\*</sup>Ru(PEt<sub>3</sub>)<sub>2</sub>Cl] (3).** To a suspension of [(Cp<sup>\*</sup>RuCl<sub>2</sub>)<sub>2</sub>] (0.85 g, 1.35 mmol) in THF (100 mL) were added PEt<sub>3</sub> (0.8 mL, 5.4 mmol) and an excess of zinc dust. The mixture was stirred for 45 min. The resulting suspension was allowed to settle, and the liquor transferred to another flask. The solvent was removed in vacuo, and the residue extracted with Et<sub>2</sub>O. Filtration, concentration, and cooling to –20 °C afforded orange crystals. Yield: 0.55 g, 80%. Anal. Calcd for C<sub>22</sub>H<sub>45</sub>ClP<sub>2</sub>Ru: C, 52.5; H, 8.01. Found: C, 52.8; H, 7.96. NMR (CDCl<sub>3</sub>) δ: (<sup>1</sup>H) 1.06 (m, PCH<sub>2</sub>CH<sub>3</sub>); 1.58 (t, J(H,P) = 2 Hz, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 1.82 (dm, PCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H}: 22.3 (s). <sup>13</sup>C{<sup>1</sup>H}: 9.2 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 10.8 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 21.3 (t, J(C,P) = 12.2 Hz, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 87.3 (t, J(C,P) = 1 Hz, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>).

**[(CpRu(PEt<sub>3</sub>)<sub>2</sub>)<sub>2</sub>(μ-S<sub>2</sub>)] [BPh<sub>4</sub>]<sub>2</sub> (4). Method A (from H<sub>2</sub>S).** To a suspension of 1 (0.13 g, 0.3 mmol) in EtOH (20 mL) was added an excess of NaBPh<sub>4</sub> (ca. 0.3 g), and then H<sub>2</sub>S was bubbled through the stirred mixture at room temperature for 2–3 min. A green precipitate was formed, which was filtered off, washed with EtOH and petroleum ether, and dried in vacuo. It was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/EtOH.

**Method B (from Elemental Sulfur).** A suspension of 1 (0.22 g, 0.5 mmol) in MeOH was treated with the stoichiometric amount of elemental sulfur (0.016 g, ca. 0.5 mmol) and an excess of NaBPh<sub>4</sub> (ca. 0.3 g), and the mixture stirred overnight. A green, microcrystalline precipitate was obtained, which was filtered off, washed with EtOH and petroleum ether, and dried. This material was recrystallized as above.

Yield: ca. 70%, for both methods. Anal. Calcd for C<sub>82</sub>H<sub>110</sub>–B<sub>2</sub>P<sub>4</sub>Ru<sub>2</sub>S<sub>2</sub>: C, 65.3; H, 7.35; S, 4.25. Found: C, 64.9; H, 7.25; S, 4.1. UV/vis (CH<sub>2</sub>Cl<sub>2</sub> solution, λ<sub>max</sub>, nm (ε, M<sup>–1</sup> cm<sup>–1</sup>)): 766–(10000), 360(6500). NMR (SO(CD<sub>3</sub>)<sub>2</sub>) δ: (<sup>1</sup>H) 1.01 (m, PCH<sub>2</sub>CH<sub>3</sub>); 1.77 (m, PCH<sub>2</sub>CH<sub>3</sub>); 5.00 (s, C<sub>5</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H}: 28.5 (s). <sup>13</sup>C{<sup>1</sup>H}: 8.3 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 21.4 (t, J(C,P) = 13.7 Hz, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 80.2 (s, C<sub>5</sub>H<sub>5</sub>).

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**[CpRu(PPh<sub>3</sub>)(P<sup>i</sup>Pr<sub>2</sub>Me)]<sub>2</sub>(μ-S<sub>2</sub>)[BPh<sub>4</sub>]<sub>2</sub> (5).** Any of the two experimental procedures described for the preparation of **4** were followed for the synthesis of this compound, starting from **2** (0.18 g, 0.3 mmol). Yield: 66–70%, for both methods. Anal. Calcd for C<sub>108</sub>H<sub>114</sub>B<sub>2</sub>P<sub>4</sub>Ru<sub>2</sub>S<sub>2</sub>: C, 71.1; H, 6.26; S, 3.52. Found: C, 70.8; H, 6.11; S, 3.4. UV/vis (CH<sub>2</sub>Cl<sub>2</sub> solution, λ<sub>max</sub>, nm (ε, M<sup>-1</sup> cm<sup>-1</sup>)): 775(18000), 355(8600). NMR (CD<sub>3</sub>COCD<sub>3</sub>) δ: (<sup>1</sup>H) 1.01 (m, P(CH<sub>3</sub>(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>)); 1.16, 1.27 (m, P(CH<sub>3</sub>(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>)); 2.42 (m, P(CH<sub>3</sub>(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>)); 4.33 (s, C<sub>5</sub>H<sub>5</sub>); 7.17, 7.60 (m, P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H}: 45.0 d, 38.6 d, J(P,P) = 40.9 Hz. <sup>13</sup>C{<sup>1</sup>H}: 2.3 (s, P(CH<sub>3</sub>(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>)); 17.2, 18.1, 18.3, 19.4 (s, P(CH<sub>3</sub>(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>)); 80.7 (t, J(C,P) = 2.2 Hz, C<sub>5</sub>H<sub>5</sub>); 124.1, 126.3, 133.9 (s, P(C<sub>6</sub>H<sub>5</sub>)).

**[Cp\*<sup>+</sup>Ru(PEt<sub>3</sub>)<sub>2</sub>(μ-S<sub>2</sub>)]<sup>-</sup>[BPh<sub>4</sub>]<sub>2</sub> (6). Method A (from H<sub>2</sub>S).** To a suspension of **3** (0.16 g, 0.3 mmol) in EtOH (20 mL) was added an excess of NaBPh<sub>4</sub> (ca. 0.3 g), and then H<sub>2</sub>S was bubbled through the stirred mixture at room temperature for 2–3 min. A mustard yellow precipitate was formed initially. Air was then admitted into the reaction mixture, and it was stirred for 24 h at room temperature. During this time, the mixture turned green. It was filtered, and the resulting green solution concentrated. Cooling to -20 °C afforded green microcrystals, which were filtered off, washed with EtOH and petroleum ether, and dried in vacuo.

**Method B (from Elemental Sulfur).** A suspension of **3** (0.25 g, 0.5 mmol) in MeOH was treated with the stoichiometric amount of elemental sulfur (0.016 g, ca. 0.5 mmol) and an excess of NaBPh<sub>4</sub> (0.3 g), and the mixture stirred overnight. A green, microcrystalline precipitate was obtained, which was filtered off, washed with EtOH and petroleum ether, and dried. Another crop was obtained from the mother liquor by concentration and cooling to -20 °C.

This material was recrystallized from acetone/EtOH or CH<sub>2</sub>-Cl<sub>2</sub>/EtOH mixtures, in the form of green needles. Yield: 45–55% for both methods. Anal. Calcd for C<sub>92</sub>H<sub>130</sub>B<sub>2</sub>P<sub>4</sub>Ru<sub>2</sub>S<sub>2</sub>: C, 67.1; H, 7.95; S, 3.9. Found: C, 67.0; H, 8.03; S, 3.7. UV/vis (CH<sub>2</sub>Cl<sub>2</sub> solution, λ<sub>max</sub>, nm (ε, M<sup>-1</sup> cm<sup>-1</sup>)): 744(6500), 398(3900). NMR (CD<sub>3</sub>COCD<sub>3</sub>) δ: (<sup>1</sup>H) 1.07 (m, PCH<sub>2</sub>CH<sub>3</sub>); 1.84 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 2.05 (dm, PCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H}: 21.2 (s). <sup>13</sup>C{<sup>1</sup>H}: 10.1 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 10.6 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 21.2 (t, J(C,P) = 13.7 Hz, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 102.8 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>).

**[Cp\*<sup>+</sup>RuH(SH)(PEt<sub>3</sub>)<sub>2</sub>][BPh<sub>4</sub>]<sup>-</sup> (7).** H<sub>2</sub>S was bubbled for 2–3 min through a solution of **3** (0.16 g, 0.3 mmol) in EtOH (20 mL) containing an excess of NaBPh<sub>4</sub> (ca. 0.3 g). Almost immediately, a mustard yellow precipitate was formed. The mixture was stirred for 15 min, and then the solids were filtered off, washed with EtOH and petroleum ether, and dried in vacuo. Yellow single crystals suitable for X-ray structure analysis were obtained by layering with EtOH a concentrated acetone solution of this compound, with careful oxygen exclusion in order to avoid the formation of the binuclear persulfide **6**. Yield: 0.14 g, 57%. Anal. Calcd for C<sub>46</sub>H<sub>67</sub>BP<sub>2</sub>RuS: C, 66.9; H, 8.18; S, 3.9. Found: C, 67.2; H, 8.33; S, 3.8. IR: ν(SH) 2670 cm<sup>-1</sup>, weak; ν(RuH) 2049 cm<sup>-1</sup>, weak. NMR (CD<sub>3</sub>-COCD<sub>3</sub>) δ: (<sup>1</sup>H) -9.67 (t, J(H,P) = 35 Hz RuH); -2.79 (t, J(H,P) = 8.4 Hz, RuSH); 1.21 (m, PCH<sub>2</sub>CH<sub>3</sub>); 1.57 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 2.01 (dm, PCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H}: 31.7 (s). <sup>13</sup>C{<sup>1</sup>H}: (CDCl<sub>3</sub>): 8.9 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 10.1 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 19.5 (t, J(C,P) = 29.6 Hz P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 103.2 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>).

**[CpRu(SNC<sub>5</sub>H<sub>5</sub>)(PEt<sub>3</sub>)<sub>2</sub>][BPh<sub>4</sub>]<sup>-</sup> (8).** To a solution of **1** (0.13 g, 0.3 mmol) in EtOH (20 mL) was added a slight excess of 2-mercaptopyridine (0.04 g, ca. 0.35 mmol). Then, an excess of NaBPh<sub>4</sub> (ca. 0.3 g) was added, and the mixture stirred for 15 min. The microcrystalline precipitate was filtered off, washed with EtOH and petroleum ether, and dried in vacuo. Yield: 0.2 g, 80%. Anal. Calcd for C<sub>46</sub>H<sub>60</sub>BNP<sub>2</sub>RuS: C, 66.3; H, 7.26; N, 1.68; S, 3.85. Found: C, 65.9; H, 7.32; N, 1.7; S, 3.8. IR: ν(NH) 3229 cm<sup>-1</sup>. NMR (CDCl<sub>3</sub>) δ: (<sup>1</sup>H) 1.02 (m, PCH<sub>2</sub>CH<sub>3</sub>), 1.75 (dm, PCH<sub>2</sub>CH<sub>3</sub>), 4.62 (s, C<sub>5</sub>H<sub>5</sub>); 6.07 (d), 6.19 (t), 6.89 (t), 7.30 (d), RuSC<sub>5</sub>H<sub>4</sub>NH; 10.04 (s br, RuSC<sub>5</sub>H<sub>4</sub>NH). <sup>31</sup>P{<sup>1</sup>H}: 28.2 (s). <sup>13</sup>C{<sup>1</sup>H}: 8.5 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 22.0 (t, J(C,P)

= 13.3 Hz, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 77.6 (s, C<sub>5</sub>H<sub>5</sub>); 114.9, 128.9, 137.4, 137.5, 173.1 (s, RuSC<sub>5</sub>H<sub>4</sub>NH).

**[CpRu(SNC<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)(P<sup>i</sup>Pr<sub>2</sub>Me)]<sup>-</sup>[BPh<sub>4</sub>]<sup>+</sup> (9).** An experimental procedure identical to that for **8** was followed for the preparation of this compound, starting from **2** (0.18 g, 0.3 mmol). Yield: 80%. Anal. Calcd for C<sub>59</sub>H<sub>62</sub>BNP<sub>2</sub>RuS: C, 71.5; H, 6.31; N, 1.41; S, 3.24. Found: C, 71.8; H, 6.36; N, 1.5; S, 3.1. IR: ν(NH) 3208 cm<sup>-1</sup>. NMR (CD<sub>3</sub>COCD<sub>3</sub>) δ: (<sup>1</sup>H) 0.27 (d, PCH<sub>3</sub>), 0.81, 1.12, 1.20 (m, P(CH(CH<sub>3</sub>)<sub>2</sub>)), 1.92 (dm, P(CH(CH<sub>3</sub>)<sub>2</sub>)), 4.72 (s, C<sub>5</sub>H<sub>5</sub>); 5.95 (m), 6.11 (t), 6.88, 7.37 (d), RuSC<sub>5</sub>H<sub>4</sub>NH; 7.28, 7.30 (m, P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>); 9.85 (s br, RuSC<sub>5</sub>H<sub>4</sub>NH). <sup>31</sup>P{<sup>1</sup>H}: 44.4 d; 33.7 d, J(P,P) = 38.5 Hz. <sup>13</sup>C{<sup>1</sup>H}: 0.17 (d, J(C,P) = 11.1 Hz, PCH<sub>3</sub>); 17.3 s, 18.6 s, 18.9 s, 19.3 (d, J(C,P) = 4.8 Hz), PCH(CH<sub>3</sub>)<sub>2</sub>); 31.0 (dd, <sup>1</sup>J(C,P) = 23.5 Hz, <sup>3</sup>J(C,P) = 2.5, PCH(CH<sub>3</sub>)<sub>2</sub>); 32.0 (dd, <sup>1</sup>J(C,P) = 24.8 Hz, <sup>3</sup>J(C,P) = 3.4 Hz, PCH(CH<sub>3</sub>)<sub>2</sub>); 81.7 (s, C<sub>5</sub>H<sub>5</sub>); 115.2, 135.7, 137.0, 137.5, 173.1 (s, RuSC<sub>5</sub>H<sub>4</sub>NH); 128.7 (s), 133.9 (d, J(C,P) = 9.80 Hz), 130.6 (s), P(C<sub>6</sub>H<sub>5</sub>).

**[Cp\*<sup>+</sup>Ru(SNC<sub>5</sub>H<sub>5</sub>)(PEt<sub>3</sub>)<sub>2</sub>][BPh<sub>4</sub>]<sup>-</sup> (10).** **10** was obtained in a fashion analogous to that for **8**, starting from **3** (0.16 g, 0.3 mmol). Yield: 0.22 g, 80%. Anal. Calcd for C<sub>51</sub>H<sub>70</sub>BNP<sub>2</sub>-RuS: C, 67.8; H, 7.76; N, 1.55; S, 3.54. Found: C, 67.9; H, 7.64; N, 1.2; S, 3.2. NMR (CD<sub>3</sub>COCD<sub>3</sub>) δ: (<sup>1</sup>H) 1.13 (m, PCH<sub>2</sub>CH<sub>3</sub>), 1.97 (dm, PCH<sub>2</sub>CH<sub>3</sub>), 1.72 (t, J(H,P) = 1 Hz, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 7.04 (t), 7.66 (d), 7.73 (d), 8.18 (t); 12.27 (s br, NH). <sup>31</sup>P{<sup>1</sup>H}: 18.2 (s). <sup>13</sup>C{<sup>1</sup>H}: 9.8 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 11.0 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 21.6 (t, J(C,P) = 12.4 Hz, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 83.8 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 116.2, 131.3, 138.6, 139.0 (s, RuSC<sub>5</sub>H<sub>4</sub>NH).

**[CpRu(S<sub>2</sub>COR)(P<sup>i</sup>Pr<sub>2</sub>Me)]<sup>-</sup> (R = Me **11a**, Et **11b**, <sup>i</sup>Pr **11c**).** To a solution of **2** (0.18 g, 0.3 mmol) in acetone (15 mL) was added the stoichiometric amount of the corresponding potassium alkylxanthate KS<sub>2</sub>COR. The resulting suspension was heated under reflux for 7 h. Then, the solvent was removed in vacuo, the residue extracted with petroleum ether, and the resulting red solution filtered through Celite. Concentration and cooling to -20 °C afforded red crystals, which were filtered off and dried. The compounds were recrystallized from petroleum ether to remove any traces of free PPh<sub>3</sub>. Yield: ca. 70% in all cases. **11a:** Anal. Calcd for C<sub>14</sub>H<sub>25</sub>OPRuS<sub>2</sub>: C, 41.5; H, 6.21; S, 15.81. Found: C, 41.2; H, 6.41; S, 15.9. IR: ν(CS) 1172, 1042 cm<sup>-1</sup>. NMR (C<sub>6</sub>D<sub>6</sub>) δ: (<sup>1</sup>H) 0.77 (d, PCH<sub>3</sub>), 0.95 (m, PCH(CH<sub>3</sub>)<sub>2</sub>), 1.68 (sept, PCH(CH<sub>3</sub>)<sub>2</sub>); 3.58 (s, OCH<sub>3</sub>); 4.43 (s, C<sub>5</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H}: 50.83 (s). <sup>13</sup>C{<sup>1</sup>H}: -1.61 (d, J(C,P) = 21.4 Hz PCH<sub>3</sub>); 18.0, 18.9 (s, PCH(CH<sub>3</sub>)<sub>2</sub>); 29.8 (d, J(C,P) = 24.8 Hz, PCH(CH<sub>3</sub>)<sub>2</sub>); 55.7 (s, OCH<sub>3</sub>); 73.6 (d, J(C,P) = 2.6 Hz, C<sub>5</sub>H<sub>5</sub>); 226.5 (d, <sup>3</sup>J(C,P) = 6 Hz, S<sub>2</sub>CO). **11b:** Anal. Calcd for C<sub>15</sub>H<sub>27</sub>OPRuS<sub>2</sub>: C, 42.9; H, 6.49; S, 15.3. Found C, 42.6; H, 6.50; S, 14.9. IR: ν(CS) 1216, 1029 cm<sup>-1</sup>. NMR (C<sub>6</sub>D<sub>6</sub>) δ: (<sup>1</sup>H) 0.81 (d, PCH<sub>3</sub>); 0.96 (t, OCH<sub>2</sub>CH<sub>3</sub>); 0.95 (m, PCH(CH<sub>3</sub>)<sub>2</sub>), 1.68 (sept, PCH(CH<sub>3</sub>)<sub>2</sub>); 4.24 (quartet, OCH<sub>2</sub>CH<sub>3</sub>); 4.45 (s, C<sub>5</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H}: 51.2 (s). <sup>13</sup>C{<sup>1</sup>H}: -2.32 (d, J(C,P) = 20.5 Hz, PCH<sub>3</sub>); 13.2 (s, OCH<sub>2</sub>CH<sub>3</sub>); 17.2, 18.2 (s, PCH(CH<sub>3</sub>)<sub>2</sub>); 29.0 (d, J(C,P) = 24.8 Hz, PCH(CH<sub>3</sub>)<sub>2</sub>); 64.7 (s, OCH<sub>2</sub>CH<sub>3</sub>); 72.8 (d, J(C,P) = 2.6 Hz, C<sub>5</sub>H<sub>5</sub>); 226.2 (d, <sup>3</sup>J(C,P) = 5.3 Hz, S<sub>2</sub>CO). **11c:** Anal. Calcd for C<sub>16</sub>H<sub>29</sub>OPRuS<sub>2</sub>: C, 44.3; H, 6.74; S, 14.7. Found C, 44.0; H, 6.64; S, 14.4. IR: ν(CS) 1215, 1098 cm<sup>-1</sup>. NMR (C<sub>6</sub>D<sub>6</sub>) δ: (<sup>1</sup>H) 0.81 (d, PCH<sub>3</sub>); 0.96 (d, OCH(CH<sub>3</sub>)<sub>2</sub>); 0.95 (m, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.67 (sept, PCH(CH<sub>3</sub>)<sub>2</sub>); 4.24 (sept, OCH(CH<sub>3</sub>)<sub>2</sub>); 4.45 (s, C<sub>5</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H}: 51.2 (s). <sup>13</sup>C{<sup>1</sup>H}: -1.5 (d, J(C,P) = 20.5 Hz, P(CH<sub>3</sub>)); 14.0 (s, OCH(CH<sub>3</sub>)<sub>2</sub>); 18.0, 19.0 (s, PCH(CH<sub>3</sub>)<sub>2</sub>); 29.9 (d, J(C,P) = 24.8 Hz, PCH(CH<sub>3</sub>)<sub>2</sub>); 65.5 (s, OCH(CH<sub>3</sub>)<sub>2</sub>); 73.6 (d, J(C,P) = 1.7 Hz, C<sub>5</sub>H<sub>5</sub>); 226.2 (d, <sup>3</sup>J(C,P) = 6 Hz, S<sub>2</sub>CO).

**[Cp\*<sup>+</sup>Ru(S<sub>2</sub>COR)(PEt<sub>3</sub>)<sub>2</sub>]<sup>-</sup> (R = Me **12a**, Et **12b**, <sup>i</sup>Pr **12c**).** An experimental procedure identical to that for **11a–c** was followed for the preparation of these complexes, starting from **3** (0.16 g, 0.3 mmol), although purification by recrystallization to achieve the removal of free PPh<sub>3</sub> was obviously not required. Yield: ca. 70% in all cases. **12a:** Anal. Calcd for C<sub>18</sub>H<sub>33</sub>-OPRuS<sub>2</sub>: C, 46.8; H, 7.16; S, 13.9. Found: C, 46.8; H, 7.29; S, 13.6. IR: ν(CS) 1216, 1046 cm<sup>-1</sup>. NMR (C<sub>6</sub>D<sub>6</sub>) δ: (<sup>1</sup>H) 0.90 (dt, PCH<sub>2</sub>CH<sub>3</sub>); 1.60 (dq, PCH<sub>2</sub>CH<sub>3</sub>); 1.71 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 3.63

(s, OCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H}: 32.9 (s). <sup>13</sup>C{<sup>1</sup>H}: 7.9 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 10.9 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 15.7 (d, J(C,P) = 22.2 Hz, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 55.9 (s, OCH<sub>3</sub>); 84.1 (d, J(C,P) = 2.6 Hz, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 228.4 (d, <sup>3</sup>J(C,P) = 6.8 Hz, S<sub>2</sub>CO). **12b**: Anal. Calcd for C<sub>19</sub>H<sub>35</sub>OPRuS<sub>2</sub>: C, 48.0; H, 7.42; S, 13.5. Found: C, 48.1; H, 7.26; S, 13.2. IR: ν(CS) 1172, 1051 cm<sup>-1</sup>. NMR (C<sub>6</sub>D<sub>6</sub>) δ: (<sup>1</sup>H) 0.92 (dt, PCH<sub>2</sub>CH<sub>3</sub>); 1.00 (t, OCH<sub>2</sub>CH<sub>3</sub>); 1.62 (dq, PCH<sub>2</sub>CH<sub>3</sub>); 1.73 (d, J(H,P) = 1.2 Hz C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 4.28 (q, OCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H}: 33.1 (s). <sup>13</sup>C{<sup>1</sup>H}: 7.9 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 10.9 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 14.0 (s, OCH<sub>2</sub>CH<sub>3</sub>); 15.8 (d, J(C,P) = 22.2 Hz, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 65.6 (OCH<sub>2</sub>CH<sub>3</sub>); 84.1 (d, J(C,P) = 1.7 Hz, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 229.8 (d, <sup>3</sup>J(C,P) = 6 Hz, S<sub>2</sub>CO). **12c**: Anal. Calcd for C<sub>20</sub>H<sub>37</sub>OPRuS<sub>2</sub>: C, 49.1; H, 7.62; S, 13.1. Found: C, 48.9; H, 7.80; S, 12.9. IR: ν(CS) 1178, 1019 cm<sup>-1</sup>. NMR (C<sub>6</sub>D<sub>6</sub>) δ: (<sup>1</sup>H) 0.91 (dt, PCH<sub>2</sub>CH<sub>3</sub>); 1.14 (d, OCH(CH<sub>3</sub>)<sub>2</sub>); 1.63 (dq, PCH<sub>2</sub>CH<sub>3</sub>); 1.74 (d, J(H,P) = 1.2 Hz C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 5.43 (septet, OCH(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H}: 33.5 (s). <sup>13</sup>C{<sup>1</sup>H}: 7.9 (s, PCH<sub>2</sub>CH<sub>3</sub>); 10.9 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 15.9 (d, J(C,P) = 22.1 Hz, PCH<sub>2</sub>CH<sub>3</sub>); 21.7 (s, OCH(CH<sub>3</sub>)<sub>2</sub>); 73.5 (s, OCH(CH<sub>3</sub>)<sub>2</sub>); 84.2 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); S<sub>2</sub>CO not observed.

**[CpRu(S<sub>2</sub>COR)(PET<sub>3</sub>)<sub>2</sub>] (R = Me **13a**, Et **13b**, <sup>i</sup>Pr **13c**).**

An experimental procedure identical to that for **11a–c** was followed for the preparation of these complexes, starting from **1** (0.13 g, 0.3 mmol) and using EtOH (20 mL) as solvent instead of acetone. Yield: ca. 75% in all cases. **13a**: Anal. Calcd for C<sub>19</sub>H<sub>38</sub>OP<sub>2</sub>RuS<sub>2</sub>: C, 44.8; H, 7.52; S, 12.6. Found: C, 44.6; H, 7.44; S, 12.4. IR: ν(CS) 1183, 1045 cm<sup>-1</sup>. NMR (C<sub>6</sub>D<sub>6</sub>) δ: (<sup>1</sup>H) 0.78 (m, PCH<sub>2</sub>CH<sub>3</sub>); 1.47 (dm, PCH<sub>2</sub>CH<sub>3</sub>); 4.09 (s, OCH<sub>3</sub>); 4.63 (s, C<sub>5</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H}: 31.9 (s). <sup>13</sup>C{<sup>1</sup>H}: 8.3 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 21.7 (t, J(C,P) = 13.1 Hz, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 58.5 (s, OCH<sub>3</sub>); 79.8 (s, C<sub>5</sub>H<sub>5</sub>); 228.9 (t, <sup>3</sup>J(C,P) = 6 Hz, S<sub>2</sub>CO). **13b**: Anal. Calcd for C<sub>20</sub>H<sub>40</sub>OP<sub>2</sub>RuS<sub>2</sub>: C, 45.9; H, 7.70; S, 12.2. Found: C, 45.9; H, 7.80; S, 11.9. IR: ν(CS) 1184, 1040 cm<sup>-1</sup>. NMR (C<sub>6</sub>D<sub>6</sub>) δ: (<sup>1</sup>H) 0.77 (m, PCH<sub>2</sub>CH<sub>3</sub>); 1.23 (t, 7.0 Hz, OCH<sub>2</sub>CH<sub>3</sub>); 1.46 (dm, PCH<sub>2</sub>CH<sub>3</sub>); 4.65 (s, C<sub>5</sub>H<sub>5</sub>); 4.76 (q, OCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H}: 31.9 (s). <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>): 8.3 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 14.5 (s, OCH<sub>2</sub>CH<sub>3</sub>); 21.6 (t, J(C,P) = 13.3 Hz, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 68.5 (s, OCH<sub>2</sub>CH<sub>3</sub>); 79.1 (s, C<sub>5</sub>H<sub>5</sub>); 229.5 (t, <sup>3</sup>J(C,P) = 6 Hz, S<sub>2</sub>CO). **13c**: Anal. Calcd for C<sub>21</sub>H<sub>42</sub>OP<sub>2</sub>RuS<sub>2</sub>: C, 46.9; H, 7.87; S, 11.9. Found: C, 46.6; H, 8.10; S, 11.7. IR: ν(CS) 1187, 1020 cm<sup>-1</sup>. NMR (C<sub>6</sub>D<sub>6</sub>) δ: (<sup>1</sup>H) 0.77 (m, PCH<sub>2</sub>CH<sub>3</sub>); 1.33 (d, OCH(CH<sub>3</sub>)<sub>2</sub>); 1.45 (dm, PCH<sub>2</sub>CH<sub>3</sub>); 4.65 (s, C<sub>5</sub>H<sub>5</sub>); 6.21 (septet, OCH(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H}: 31.9 (s). <sup>13</sup>C{<sup>1</sup>H}: 8.4 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 22.0 (t, J(C,P) = 12.4 Hz, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 22.6 (s, OCH(CH<sub>3</sub>)<sub>2</sub>); 74.9 (s, OCH(CH<sub>3</sub>)<sub>2</sub>); 79.7 (s, C<sub>5</sub>H<sub>5</sub>); 227.7 (t, <sup>3</sup>J(C,P) = 6 Hz, S<sub>2</sub>CO).

**[CpRu(S<sub>2</sub>CNEt<sub>2</sub>)(P<sup>i</sup>Pr<sub>2</sub>Me)] (**14**).** A solution of **2** (0.15 g, 0.25 mmol) in acetone (15 mL) was treated with sodium diethyldithiocarbamate (0.25 mmol), and the resulting suspension heated under reflux for 7 h. The solvent was removed in vacuo and the residue was extracted with petroleum ether and filtered through Celite. Concentration and cooling to -20 °C afforded red-brown crystals, which were recrystallized from petroleum ether in order to remove traces of free PPh<sub>3</sub>. Yield: 80%. Anal. Calcd for C<sub>17</sub>H<sub>32</sub>NPRuS<sub>2</sub>: C, 45.7; H, 7.22; N, 3.1; S, 14.4. Found: C, 45.9; H, 7.11; N 3.1; S, 14.6. IR: ν(C=N) 1457 cm<sup>-1</sup>. NMR (CDCl<sub>3</sub>) δ: (<sup>1</sup>H) 0.90 (t, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>); 1.05 (d, PCH<sub>3</sub>); 1.07 (m, PCH(CH<sub>3</sub>)<sub>2</sub>); 3.24, 3.40 (m, NCH<sub>2</sub>CH<sub>3</sub>); 1.87 (septet, PCH(CH<sub>3</sub>)<sub>2</sub>); 4.35 (s, C<sub>5</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H}: 52.09 (s). <sup>13</sup>C{<sup>1</sup>H}: -1.05 (d, J(C,P) = 5.6 Hz, PCH<sub>3</sub>); 12.7 (s, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>); 18.2, 19.1 (s, PCH(CH<sub>3</sub>)<sub>2</sub>); 30.2 (d, J(C,P) = 23.2 Hz, PCH(CH<sub>3</sub>)<sub>2</sub>); 42.54, 42.76 (s, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>); 73.9 (d, J(C,P) = 1.7 Hz, C<sub>5</sub>H<sub>5</sub>).

**[Cp\*<sup>+</sup>Ru(S<sub>2</sub>CNEt<sub>2</sub>)(PET<sub>3</sub>)<sub>3</sub>] (**15**).** Brown crystals of **15** were obtained in a fashion analogous to that for **14**, starting from **3** (0.13 g, 0.25 mmol) and omitting the separation from free PPh<sub>3</sub>. Yield: 0.1 g, 80%. Anal. Calcd for C<sub>21</sub>H<sub>40</sub>NPRuS<sub>2</sub>: C, 50.2; H, 8.02; N, 2.8; S, 12.7. Found: C, 50.0; H, 8.00; N, 2.9; S, 12.5. IR: ν(C=N) 1478 cm<sup>-1</sup>. NMR (C<sub>6</sub>D<sub>6</sub>) δ: (<sup>1</sup>H) 0.95 (t, NCH<sub>2</sub>CH<sub>3</sub>); 0.99 (dt, PCH<sub>2</sub>CH<sub>3</sub>); 1.78 (dq, PCH<sub>2</sub>CH<sub>3</sub>); 1.82 (t, J(H,P) = 1 Hz, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 3.31, 3.43 (m, NCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H}: 33.8 (s). <sup>13</sup>C{<sup>1</sup>H}: 8.1 (s, PCH<sub>2</sub>CH<sub>3</sub>); 10.9, 12.6 (s, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>);

**Table 1. Summary of Data for the Crystal Structure Analysis of **7** and **12c****

|   | <b>7</b>  | <b>12c</b>  |
|---|---|---|
| formula   | C <sub>46</sub> H <sub>67</sub> B <sub>P</sub> <sub>2</sub> RuS | C <sub>20</sub> H <sub>37</sub> OPRuS <sub>2</sub>  |
| fw  | 825.88  | 489.68  |
| crystal size (mm)   | 0.12 × 0.15 × 0.32  | 0.35 × 0.23 × 0.40  |
| crystal system  | orthorhombic  | triclinic   |
| space group   | P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)          | P-1 (No. 2)   |
| cell parameters   | a = 16.042(3) Å<br>b = 20.451(5) Å<br>c = 13.282(4) Å           | a = 8.884(6) Å<br>b = 15.960(8) Å<br>c = 8.711(6) Å<br>α = 91.66(5)°<br>β = 104.95(5)°<br>γ = 87.65(5)° |
| volume  | 4358(2) Å <sup>3</sup>  | 1192(2)   |
| Z   | 4   | 2   |
| ρ <sub>calcd</sub>  | 1.251 g cm <sup>-3</sup>  | 1.364 g cm <sup>-3</sup>  |
| λ(Mo Kα)  | 0.71069 Å   | 0.71069 Å   |
| μ(Mo Kα)  | 4.99 cm <sup>-1</sup>   | 8.85 cm <sup>-1</sup>   |
| F(000)  | 1732  | 512   |
| transmission factors  | 0.94–1.00   | 0.76–1.00   |
| scan speed (ω)  | 4° min <sup>-1</sup>  | 4° min <sup>-1</sup>  |
| 2θ interval   | 5° < 2θ < 50.1°   | 5° < 2θ < 50.1°   |
| no. of measd reflns   | 3680  | 4095  |
| no. of unique reflns  | 3539  | 3853  |
| no. of obsd reflns  | 1841 (I > 2σ <sub>I</sub> )                                     | 3253 (I > 3σ <sub>I</sub> )   |
| no. of params   | 229   | 226   |
| reflection/parameter ratio                                      | 8.04  | 14.39   |
| R <sup>a</sup>  | 0.076   | 0.041   |
| R <sub>w</sub> (w = σ <sub>F</sub> <sup>-2</sup> ) <sup>b</sup> | 0.088   | 0.051   |
| max Δ/σ in final cycle  | 4.52  | 2.77  |
| GOF   | 1.98  | 1.98  |

$$^a R = \sum |F_o| - |F_c| / \sum |F_o|. \quad ^b R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$$

11.9 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 16.3 (d, J(C,P) = 21.4 Hz, PCH<sub>2</sub>CH<sub>3</sub>); 42.8, 49.1 (s, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>); 83.8 (d, J(C,P) = 3.5 Hz, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>).

**[CpRu(S<sub>2</sub>CNEt<sub>2</sub>)(PET<sub>3</sub>)<sub>2</sub>] (**16**).** **16** was obtained in the form of orange crystals following a procedure identical to that for **14**, starting from **1** (0.11 g, 0.25 mmol). Yield: 0.11 g, 80%. Anal. Calcd for C<sub>22</sub>H<sub>45</sub>NP<sub>2</sub>RuS<sub>2</sub>: C, 48.0; H, 8.24; N, 2.5; S, 11.6. Found: C, 47.8; H, 8.11; N, 2.63; S, 11.5. IR: ν(C=N) 1481 cm<sup>-1</sup>. NMR (C<sub>6</sub>D<sub>6</sub>) δ: (<sup>1</sup>H) 0.68 (t, NCH<sub>2</sub>CH<sub>3</sub>); 0.92 (m, PCH<sub>2</sub>CH<sub>3</sub>); 1.57 (dm, PCH<sub>2</sub>CH<sub>3</sub>); 3.01, 3.61 (m, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>); 4.38 (s, C<sub>5</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H}: 32.7 (s). <sup>13</sup>C{<sup>1</sup>H}: 8.3 (s, PCH<sub>2</sub>CH<sub>3</sub>); 11.5, 12.3 (s, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>); 21.2 (t, J(C,P) = 12.4 Hz, PCH<sub>2</sub>CH<sub>3</sub>); 46.5, 49.6 (s, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>); 76.9 (t, J(C,P) = 2.6 Hz, C<sub>5</sub>H<sub>5</sub>).

**Experimental Data for the X-ray Crystal Structure Determinations.** Crystals suitable for X-ray diffraction analysis were mounted onto a glass fiber and transferred to an AFC6S-Rigaku automatic diffractometer (T = 290 K, Mo Kα radiation, graphite monochromator, λ = 0.710 73 Å). Accurate unit cell parameters and an orientation matrix in each case were determined by least-squares fitting from the settings of 25 high-angle reflections. Crystal data and details on data collection and refinements are given in Table 1. Data were collected by the ω-2θ scan method in both cases. Lorentz and polarization corrections were applied. Decay was monitored by measuring three standard reflections every 100 measurements. Decay and semiempirical absorption correction (ψ method) were also applied.

The structures were solved by Patterson methods and subsequent expansion of the models using DIRDIF.<sup>20</sup> Reflections having I > 2σ(I) in the case of complex **7** or I > 3σ(I) in the case of complex **12c** were used for structure refinement. For **7**, Ru, S, and P atoms were anisotropically refined, and the remaining non-H atoms were isotropically refined. Some disorder was detected in ethyl groups, and C(20) was refined in two positions with complementary population factors. H-(1) and H(2) were localized in difference Fourier maps, and

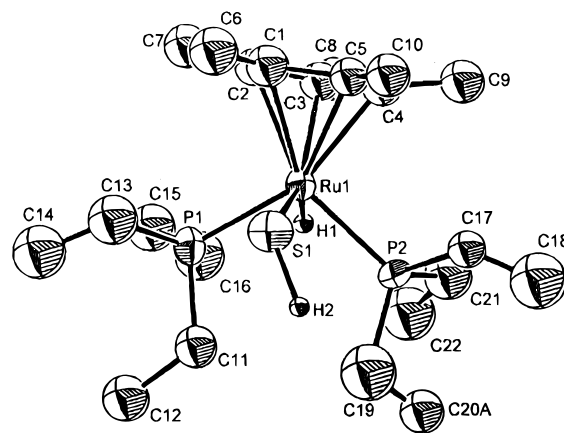
(20) Beurkens, P. T. *DIRDIF*, Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 6525 Ed Nijmegen, Netherlands.

the remaining H atoms included at idealized positions. For **12c** all non-H atoms were anisotropically refined, and the H atoms were included at idealized positions. H atoms were not refined. All calculations for data reduction, structure solution, and refinement were carried out on a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using the TEXSAN<sup>21</sup> software system and ORTEP<sup>22</sup> for plotting. Maximum and minimum peaks in the final difference Fourier maps were +1.01 and  $-0.61 \text{ e } \text{Å}^{-3}$  for **7** and +1.01 and  $-1.15 \text{ e } \text{Å}^{-3}$  for **12c**.

## Results and Discussion

The complexes  $[\text{CpRuCl}(\text{PET}_3)_2]$  (**1**) and  $[\text{CpRuCl}(\text{PPh}_3)(\text{PMe}_2\text{Pr}_2)]$  (**2**) react with  $\text{H}_2\text{S}$  in EtOH in the presence of NaBPh<sub>4</sub> furnishing the deep green persulfido complexes  $[\{\text{CpRu}(\text{PET}_3)_2\}_2(\mu\text{-S}_2)][\text{BPh}_4]_2$  (**4**) and  $[\{\text{CpRu}(\text{PPh}_3)(\text{PMe}_2\text{Pr}_2)_2(\mu\text{-S}_2)][\text{BPh}_4]_2$  (**5**), respectively. These compounds are also accessible by reaction of **1** or **2** with the stoichiometric amount of elemental sulfur and an excess of NaBPh<sub>4</sub> in MeOH, a procedure developed by Rauchfuss and co-workers for the preparation of a range of binuclear half-sandwich persulfide complexes of ruthenium.<sup>23</sup> The spectral properties of **4** and **5** match those reported for the complexes  $[\{\text{CpRu}(\text{L})_2\}_2(\mu\text{-S}_2)]^{2+}$  (Cp = C<sub>5</sub>H<sub>5</sub>, C<sub>5</sub>H<sub>4</sub>Me; L = PPh<sub>3</sub>, PMe<sub>3</sub>),<sup>23</sup> including the presence of a strong charge-transfer band near 750 nm in the visible spectrum, ascribed to transitions involving the Ru<sub>2</sub>S<sub>2</sub> core and responsible for the intense green color displayed by these compounds.<sup>24</sup> On these grounds, the structure of these persulfide complexes is probably analogous to that found by X-ray crystallography for  $[\{\text{CpRu}(\text{PMe}_3)_2\}_2(\mu\text{-S}_2)][\text{SbF}_6]_2 \cdot 2 \text{C}_6\text{H}_5\text{NO}_2$ , which consists of a centrosymmetrical arrangement of  $\{\text{CpRu}(\text{PMe}_3)_2\}$  moieties linked by a persulfido unit.<sup>23</sup>

The reaction of the pentamethylcyclopentadienyl derivative  $[\text{Cp}^*\text{RuCl}(\text{PET}_3)_2]$  (**3**) with elemental sulfur and NaBPh<sub>4</sub> in MeOH also yielded, as expected, the binuclear persulfido complex  $[\{\text{Cp}^*\text{Ru}(\text{PET}_3)_2\}_2(\mu\text{-S}_2)][\text{BPh}_4]_2$  (**6**). However, the direct reaction of **3** with  $\text{H}_2\text{S}$  followed a different course. Thus, when  $\text{H}_2\text{S}$  was bubbled through a slurry of **3** in EtOH containing an excess of NaBPh<sub>4</sub>, a mustard yellow precipitate was immediately obtained, which upon isolation turned to be the Ru<sup>IV</sup> hydrido-metallothiol complex  $[\text{Cp}^*\text{RuH}(\text{SH})(\text{PET}_3)_2][\text{BPh}_4]$  (**7**). This compound is diamagnetic, as inferred from NMR data, and shows weak  $\nu(\text{SH})$  and  $\nu(\text{RuH})$  bands at 2670 and 2049  $\text{cm}^{-1}$  in its IR spectrum. The resonances for the hydrido and mercapto protons appear as triplets at  $-9.67 \text{ ppm}$  ( $^2J(\text{H,P}) = 35 \text{ Hz}$ ) and  $-2.79 \text{ ppm}$  ( $^3J(\text{H,P}) = 8.4 \text{ Hz}$ ), respectively, in the <sup>1</sup>H NMR spectrum, whereas the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum consists of one singlet. These spectral data suggest a four-legged piano stool structure for the complex cation. This was unequivocally established by X-ray crystal structure analysis. An ORTEP view of  $[\text{Cp}^*\text{RuH}(\text{SH})(\text{PET}_3)_2]^+$  is shown in Figure 1. Selected bond lengths and angles are listed in Table 2. The coordination



**Figure 1.** ORTEP drawing of the cation  $[\text{Cp}^*\text{RuH}(\text{SH})(\text{PET}_3)_2]^+$  with 50% probability thermal ellipsoids. H atoms, except hydride and that on the mercapto ligand, are omitted.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for  $[\text{Cp}^*\text{RuH}(\text{SH})(\text{PET}_3)_2][\text{BPh}_4]$  (**7**) with Estimated Standard Deviations in Parentheses

|                 |          |                 |          |
|-----------------|----------|-----------------|----------|
| Ru(1)–S(1)      | 2.411(6) | Ru(1)–C(3)      | 2.31(3)  |
| Ru(1)–P(1)      | 2.341(6) | Ru(1)–C(4)      | 2.34(3)  |
| Ru(1)–P(2)      | 2.334(7) | Ru(1)–C(5)      | 2.37(3)  |
| Ru(1)–C(1)      | 2.35(3)  | Ru(1)–H(1)      | 1.50     |
| Ru(1)–C(2)      | 2.37(2)  | S(1)–H(2)       | 1.56     |
| S(1)–Ru(1)–P(1) | 83.0(3)  | P(1)–Ru(1)–C(4) | 150.1(7) |
| S(1)–Ru(1)–P(2) | 83.4(3)  | P(1)–Ru(1)–C(5) | 144.0(7) |
| S(1)–Ru(1)–C(1) | 90.1(7)  | P(2)–Ru(1)–C(1) | 143.6(7) |
| S(1)–Ru(1)–C(2) | 119.4(6) | P(2)–Ru(1)–C(2) | 151.2(6) |
| S(1)–Ru(1)–C(3) | 145.6(6) | P(2)–Ru(1)–C(3) | 118.6(7) |
| S(1)–Ru(1)–C(4) | 120.4(7) | P(2)–Ru(1)–C(4) | 94.4(7)  |
| S(1)–Ru(1)–C(5) | 87.9(7)  | P(2)–Ru(1)–C(5) | 105.9(7) |
| P(1)–Ru(1)–P(2) | 107.5(2) | S(1)–Ru(1)–H(1) | 131.33   |
| P(1)–Ru(1)–C(1) | 107.2(7) | P(1)–Ru(1)–H(1) | 66.40    |
| P(1)–Ru(1)–C(2) | 93.6(7)  | P(2)–Ru(1)–H(1) | 71.96    |
| P(1)–Ru(1)–C(3) | 111.5(6) | Ru(1)–S(1)–H(2) | 123.97   |

around ruthenium can be described as a four-legged piano stool structure. The hydride and mercapto ligands are in mutually transoid positions, with an H(1)–Ru–S(1) angle of 131.33°. The phosphines also adopt a transoid disposition with a P(1)–Ru–P(2) angle of 107.5(2)°. The ruthenium–hydride bond distance Ru–H(1) 1.50 Å is in the normal range previously observed in other ruthenium hydride complexes.<sup>25</sup> The Ru–S(1) separation 2.411(6) Å is slightly shorter than in  $[\text{Ru}(\text{SH})_2(\text{CO})_2(\text{PPh}_3)_2]$  (2.472(2) and 2.470(2) Å),<sup>5</sup> possibly due to the fact that in the latter complex the mercapto groups are trans to strong  $\pi$ -acceptor CO ligands, but other ruthenium complexes with thiolato ligands show Ru–S separations in the range 2.40–2.43 Å,<sup>26</sup> fully consistent with the value observed by us. The hydrogen atom attached to sulfur was located in a difference Fourier map but not refined, resulting in a S(1)–H(2) bond distance of 1.56 Å and a Ru–S(1)–H(2) angle of 123.97°. This S–H bond length is longer than found in gaseous  $\text{H}_2\text{S}$  (1.33 Å) and also in the reported terminal mercapto complexes with located protons (1.2–1.4 Å), the Ru–S(1)–H(2) angle being also larger than in other

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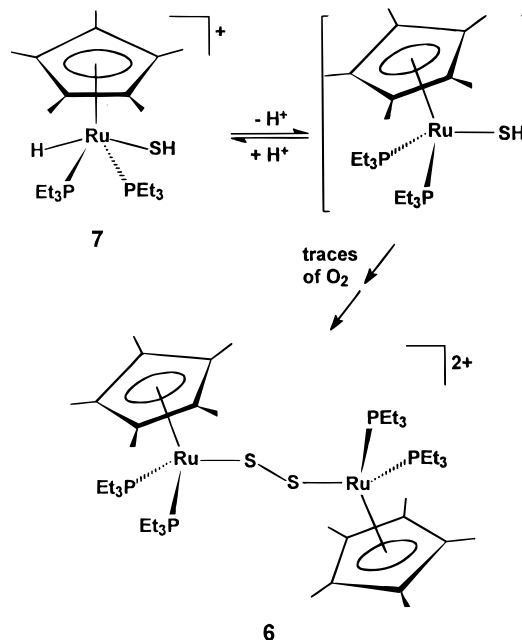
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complexes (usually less than  $100^\circ$ ), although approaching those in  $[\text{Cp}^*\text{Ti}(\text{SH})_2]$  ( $106^\circ$  and  $116^\circ$ ).<sup>27</sup> It has been suggested that more electropositive atoms, such as  $\text{Ti}^{\text{IV}}$ , attached to sulfur cause wider angles at the S,<sup>5</sup> an observation consistent with the fact that compound **7** contains a ruthenium atom in the high formal oxidation state +4. The C5 ring of the  $\text{C}_5\text{Me}_5$  ligand is planar, and the plane defined by the  $\text{C}_5\text{Me}_5$  centroid, the hydride, S(1), and the metal atom is nearly normal to the C5 ring, an arrangement that has been previously observed in other half-sandwich  $\text{Ru}^{\text{IV}}$  complexes such as  $[\text{Cp}^*\text{Ru}(\text{H})_2(\text{dippe})][\text{BPh}_4]^{28}$  and  $[\text{Cp}^*\text{RuH}(\text{C}\equiv\text{CCOOMe})(\text{dippe})][\text{BPh}_4]$  (dippe = 1,2-bis(diisopropylphosphino)ethane).<sup>29</sup> All the other bond lengths and angles found in the ligands and in the  $[\text{BPh}_4]^-$  anion are in the usual range.

Although oxidative addition of  $\text{H}_2\text{S}$  to transition metal complexes is well established,<sup>5,8,14,15</sup> this is the first case, as far as we are aware, in which the formal oxidation from  $\text{Ru}^{\text{II}}$  to  $\text{Ru}^{\text{IV}}$  has been observed. This process resembles the oxidative addition of  $\text{H}_2$  to  $[\text{CpRu}(\text{PR}_3)_2]^+$  fragments to yield the corresponding  $\text{Ru}^{\text{IV}}$  dihydrides  $[\text{CpRu}(\text{H})_2(\text{PR}_3)_2]^+$ <sup>28</sup> or even the recently reported oxidative addition of 1-alkynes to  $[\text{Cp}^*\text{Ru}(\text{dippe})]^+$  to furnish  $\text{Ru}^{\text{IV}}$  hydrido-alkynyl complexes  $[\text{Cp}^*\text{RuH}(\text{C}\equiv\text{CR})(\text{dippe})]^+$ , intermediates in the formation of the corresponding vinylidene derivatives  $[\text{Cp}^*\text{Ru}=\text{C}=\text{CHR}(\text{dippe})]^+$ .<sup>29</sup> Once more, the differences between cyclopentadienyl ruthenium complexes and their pentamethylcyclopentadienyl analogues become apparent, since no hydrido-metallothiol complexes have been observed in the course of the reaction of **1** or **2** with  $\text{H}_2\text{S}$ . Pentamethylcyclopentadienyl ruthenium complexes contain metal centers that are more electron-rich than those in its cyclopentadienyl counterparts, owing to the increased electron-releasing capabilities of the  $\text{C}_5\text{Me}_5$  in comparison with  $\text{C}_5\text{H}_5$ .

Compound **7** is slowly oxidized in solution by atmospheric oxygen to yield the green persulfido complex **6**, with concomitant formation of water. In fact, if a slurry of **7** in MeOH or EtOH is stirred overnight in air at room temperature, it gradually turns green, and finally **6** is obtained. Compound **6** is also recovered in poor yields from the mother liquor of the reaction of **3** with  $\text{H}_2\text{S}$  in EtOH. We can tentatively propose the reaction sequence shown in Scheme 1 to explain the formation of **6** at the expense of **7**. The hydrido-metallothiol complex **7** is possibly in equilibrium with the neutral mercapto derivative  $[\text{Cp}^*\text{Ru}(\text{SH})(\text{PET}_3)_2]$ , as a result of a deprotonation/reprotonation process. Since neutral mercapto complexes of ruthenium such as  $[\text{CpRu}(\text{SH})(\text{PPh}_3)_2]$  are known to undergo easy oxidation to yield the corresponding binuclear persulfido derivatives,<sup>10</sup> this may also happen in our case even at trace level concentrations of  $\text{O}_2$ . Another feasible pathway should involve protonation of the putative mercapto complex at the lone pair of sulfur to give the  $\text{H}_2\text{S}$  adduct  $[\text{Cp}^*\text{Ru}(\text{SH}_2)(\text{PET}_3)_2]^+$ , which according to data in the literature should be an unstable species easily oxidizable to the

### Scheme 1. Proposed Reaction Sequence for the Formation of the Binuclear Persulfide Complex **6** at the Expense of the Hydrido-Metallothiol **7**



corresponding persulfido species **6**.<sup>10,12</sup> Experimental evidence supporting the occurrence of a deprotonation/reprotonation equilibrium comes from the observation that the hydride ligand readily exchanges with deuterium when  $\text{D}_2\text{O}$  is added to an acetone solution of **7**, furnishing the isotopomer  $[\text{Cp}^*\text{RuD}(\text{SH})(\text{PET}_3)_2]^+$  as inferred from NMR spectroscopy. Under these conditions, no deuterium exchange with the mercapto proton is observed, at variance with what happens in the case of  $[\text{RuH}(\text{SH})(\text{CO})_2(\text{PPh}_3)_2]$ , for which the exchange at the hydride occurs more slowly than that at the mercapto moiety.<sup>5</sup> This difference is possibly due to the fact that compound **7** is relatively acidic due to its cationic nature and also because it contains  $\text{Ru}^{\text{IV}}$ , whereas  $[\text{RuH}(\text{SH})(\text{CO})_2(\text{PPh}_3)_2]$  is a neutral  $\text{Ru}^{\text{II}}$  derivative, with fairly basic properties.<sup>5</sup> Although the reaction sequence shown in Scheme 1 seems reasonable, it must be regarded with due caution, since attempts made to isolate the neutral mercapto complex  $[\text{Cp}^*\text{Ru}(\text{SH})(\text{PET}_3)_2]$  have been so far unsuccessful, and no direct spectral evidence could be obtained for this intermediate. Accordingly, other possible reaction pathways cannot be ruled out.

The reaction of half-sandwich ruthenium complexes with organic thiols has been reported to produce thiolate complexes, or even thiol derivatives,<sup>30</sup> i.e.,  $[\text{CpRu}(\text{HSBu})(\text{dppm})][\text{PF}_6]$ , which have shown to be extremely air-sensitive. However in our case, the reactions of **1**, **2**, and **3** with organic thiols such as HSPH in MeOH in the presence of  $\text{NaBPh}_4$  produced complex mixtures from which no pure compound was isolated. In contrast with this, the reaction with 2-mercaptopyridine (HSPy) allowed the isolation of red-orange microcrystalline materials. No bands attributable to  $\nu(\text{SH})$  or  $\nu(\text{RuH})$  were observed in the IR spectrum of these compounds. Instead, one medium band near  $3200\text{ cm}^{-1}$ , assigned to

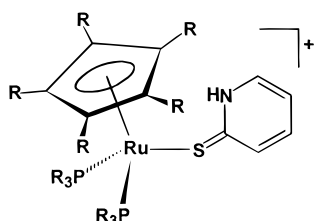
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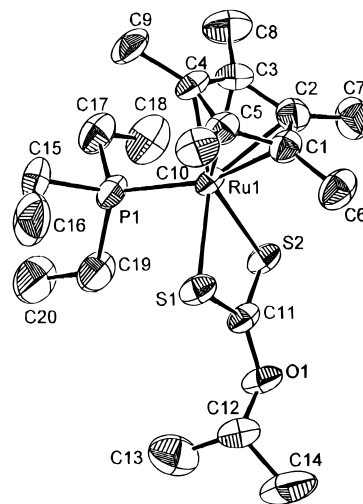
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$\nu(\text{NH})$ , was present. This band is consistent with the presence of one broad resonance in the range 10–12 ppm in their  $^1\text{H}$  NMR spectra, attributable to nitrogen-bound protons, suggesting that HSPy exists as its 1H-pyridine-2-thione tautomeric form  $\text{S}=\text{CCH}=\text{CHCH}=\text{CHNH}$  in these complexes, which according to microanalysis can hence be formulated as  $[\text{CpRu}(\text{S}=\text{CCH}=\text{CHCH}=\text{CHNH})(\text{PEt}_3)_2][\text{BPh}_4]$  (**8**),  $[\text{CpRu}(\text{S}=\text{CCH}=\text{CH}-\text{CH}=\text{CHNH})(\text{PPh}_3)(\text{PMe}^i\text{Pr}_2)][\text{BPh}_4]$  (**9**), and  $[\text{Cp}^*\text{Ru}(\text{S}=\text{CCH}=\text{CHCH}=\text{CHNH})(\text{PEt}_3)_2][\text{BPh}_4]$  (**10**), respectively. NMR spectral data suggest for these compounds a typical three-legged piano stool structures, with the 1H-pyridinethione ligand attached to the metal through the sulfur atom, as shown:



R = H;  $\text{PR}_3 = \text{PEt}_3$  **8**  
 R = H;  $\text{PR}_3 = \text{PPh}_3, \text{PMe}^i\text{Pr}_2$  **9**  
 R = Me;  $\text{PR}_3 = \text{PEt}_3$  **10**

The tautomeric processes in 2-mercaptopyridine are well established.<sup>31,32</sup> In fact, the mercaptopyridine in its free form exists predominantly as 1H-pyridinethione, and coordinates as such through the sulfur atom, as in our case. HSPy may also coordinate as the conjugate anion pyridine-2-thiolate,  $\text{PyS}^-$ , in various ways which include S-monodentate, S,N-bidentate or even bridging.<sup>17,31,32</sup> Attempts made to obtain neutral  $\eta^1$ - or  $\eta^2$ -pyridinethiolate complexes by deprotonation of **8–10** were unsuccessful. However, we succeeded in preparing a range of neutral derivatives containing alkylxanthates or diethyldithiocarbamate as ligands, these acting as  $\eta^1$ - or  $\eta^2$ -depending upon the particular complex. Thus, the metathetical exchange reaction of **2** and **3** with potassium alkylxanthates  $\text{KS}_2\text{COR}$  (R = Me, Et,  $^i\text{Pr}$ ) in refluxing EtOH afforded the neutral chelate complexes  $[\text{CpRu}(\eta^2\text{-S}_2\text{COR})(\text{PMe}^i\text{Pr}_2)]$  (R = Me **11a**, Et **11b**,  $^i\text{Pr}$  **11c**) and  $[\text{Cp}^*\text{Ru}(\eta^2\text{-S}_2\text{COR})(\text{PEt}_3)]$  (R = Me **12a**, Et **12b**,  $^i\text{Pr}$  **12c**), respectively. However, when the same reactions were performed starting from **1**, the isolated products  $[\text{CpRu}(\eta^1\text{-S}_2\text{COR})(\text{PEt}_3)_2]$  (R = Me **13a**, Et **13b**,  $^i\text{Pr}$  **13c**) contained the xanthate bound as monodentate. In analogous fashion, the reaction of **2** and **3** with sodium diethyldithiocarbamate in acetone under reflux yielded the corresponding chelate complexes  $[\text{CpRu}(\eta^2\text{-S}_2\text{CNET}_2)(\text{PMe}^i\text{Pr}_2)]$  (**14**) and  $[\text{Cp}^*\text{Ru}(\eta^2\text{-S}_2\text{CNET}_2)(\text{PEt}_3)]$  (**15**), whereas from the reaction of **1**,  $[\text{CpRu}(\eta^1\text{-S}_2\text{-CNET}_2)(\text{PEt}_3)_2]$  (**16**) was obtained. The IR spectra of all these derivatives show the characteristic bands associated with xanthate or dithiocarbamate ligands, although the values found for  $\nu(\text{CS})$ , as well as for  $\nu(\text{CN})$  in the



**Figure 2.** ORTEP drawing (50% probability thermal ellipsoids) of  $[\text{Cp}^*\text{Ru}(\text{S}_2\text{CO}^i\text{Pr})(\text{PEt}_3)]$ . H atoms are omitted.

dithiocarbamate complexes, are too ambiguous to allow unequivocal distinction between  $\eta^1$ - and  $\eta^2$ -coordination. The  $^1\text{H}$  NMR spectra of all these compounds display one single  $\text{C}_5\text{H}_5$  or  $\text{C}_5\text{Me}_5$  resonance, together with the signals corresponding to the phosphine protons plus those of the R group in the xanthate, or ethyl protons in the dithiocarbamate. In all cases, one singlet is observed in their  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra. Apart from microanalysis, the distinction between  $\eta^1$ - and  $\eta^2$ -coordination for the xanthate or dithiocarbamate ligands can be made on the basis of the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra. All compounds containing a bidentate xanthate or dithiocarbamate have lost one phosphine, and therefore the resonances for the carbon atoms directly attached to phosphorus appear as doublets. However, when the coordination is  $\eta^1$ , the corresponding complex contains two phosphine ligands, and the resonances for the phosphorus-bound carbon atoms appear as virtual triplets. In xanthate complexes, the resonance of the  $\text{CS}_2$  quaternary carbon, when observed, also allows discrimination between  $\eta^1$ - and  $\eta^2$ -coordination, since coupling with phosphorus is frequently observed; hence one triplet indicates the presence of two phosphorus atoms in the complex, as it occurs for compounds **13a–c**, whereas for complexes containing one phosphine ligand the  $\text{CS}_2$  resonance appears as one doublet. For dithiocarbamate complexes **14**, **15**, and **16** such resonance has not been detected, possibly because of the quadrupolar  $^{14}\text{N}$  nucleus.

The crystal structure of compound **12c** was determined. An ORTEP view of the molecule is shown in Figure 2. Selected bond lengths and angles are listed in Table 3. The crystal contains discrete neutral molecules with a pseudooctahedral three-legged piano stool structure, in which three of the positions are occupied by the  $\text{C}_5\text{Me}_5$  ring, one by the phosphine ligand, and the remaining two by the sulfur atoms of the xanthate moiety. This arrangement is essentially identical to that observed for the thioxanthate complex  $[\text{CpRu}(\text{S}_2\text{CSP}^n)(\text{PPh}_3)]$ .<sup>33</sup> The  $\text{S}_2\text{CO}$  unit of the xanthate is planar, with angles around C(11) consistent with an  $\text{sp}^2$  hybridization. The Ru–S and C–S separa-

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**Table 3. Selected Bond Lengths (Å) and Angles (deg) for [Cp\*Ru(S<sub>2</sub>CO<sup>+</sup>Pr)(PEt<sub>3</sub>)] (12c) with Estimated Standard Deviations in Parentheses.**

|                  |          |                  |          |
|------------------|----------|------------------|----------|
| Ru(1)–S(1)       | 2.393(2) | Ru(1)–C(4)       | 2.194(5) |
| Ru(1)–S(1)       | 2.406(2) | Ru(1)–C(5)       | 2.181(5) |
| Ru(1)–P(1)       | 2.301(2) | S(1)–C(11)       | 1.682(5) |
| Ru(1)–C(1)       | 2.198(5) | S(2)–C(11)       | 1.678(5) |
| Ru(1)–C(2)       | 2.192(5) | O(1)–C(11)       | 1.315(6) |
| Ru(1)–C(3)       | 2.197(5) | O(1)–C(12)       | 1.475(7) |
| S(1)–Ru(1)–S(2)  | 71.45(6) | C(11)–O(1)–C(12) | 119.6(4) |
| S(1)–Ru(1)–P(1)  | 90.84(8) | S(1)–C(11)–S(2)  | 113.0(3) |
| S(2)–Ru(1)–P(1)  | 92.52(7) | S(1)–C(11)–O(1)  | 126.9(4) |
| Ru(1)–S(1)–C(11) | 87.9(2)  | S(2)–C(11)–O(1)  | 120.1(4) |
| Ru(1)–S(2)–C(11) | 87.6(2)  |                  |          |

tions are very similar, suggesting an essentially symmetrical chelating mode for the xanthate, and consistent with values found in the literature for other ruthenium xanthate<sup>34</sup> and thioxanthate<sup>33</sup> complexes. All the other distances and angles in the C<sub>5</sub>Me<sub>5</sub> and phosphine ligand are in the normal range and do not require further comments.

It is interesting that in the series of xanthate and dithiocarbamate complexes described in this work, the  $\eta^1$ -coordination has only been observed in cyclopentadienylbis(triethylphosphine) derivatives. Clearly, complexes containing monodentate xanthate or dithiocarbamate must be intermediates in the formation of the corresponding chelate species, as has been proposed for the reaction of [RuCl<sub>2</sub>(L)<sub>3</sub>] (L = PPh<sub>3</sub>, PEtPh<sub>2</sub>, P(OMe)Ph<sub>2</sub>, P(OEt)Ph<sub>2</sub>) and [RuCl<sub>2</sub>(L)<sub>4</sub>] (L = PPh(OMe)<sub>2</sub>, PMe<sub>2</sub>Ph, PMePh<sub>2</sub>) with alkali metal salts of several dithio acids such as xanthates and dithiocarbamates (S–S), to give [Ru{ $\eta^2$ -(S–S)}<sub>2</sub>(L)<sub>2</sub>] derivatives.<sup>35</sup> The chelate ring closure reaction is an entropy-driven, thermally

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favored process, but in our system it involves the elimination of one phosphine ligand. Thus, the formation of the chelate ring must compensate the loss of a metal–phosphorus bond. This happens with relative ease if one of the phosphine ligands is labile, e.g., PPh<sub>3</sub> in complex **2** or PEt<sub>3</sub> in **3**. The fact that PEt<sub>3</sub> is labile in **3** but not in **1** is possibly due to the stronger electron-releasing properties of the C<sub>5</sub>Me<sub>5</sub> ligand compared to C<sub>5</sub>H<sub>5</sub>, which may help in the stabilization of 16-electron species formed upon phosphine dissociation<sup>36</sup> prior to chelate ring closure. Subsequent attack of the released phosphine to the ROCS<sub>2</sub> carbon atom of the xanthate ligand has not been observed. Such a process leads to zwitterionic species of the type S<sub>2</sub>C<sup>−</sup>(P<sup>+</sup>R<sub>3</sub>)OR, and this has been reported to occur in some instances.<sup>37</sup>

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**Supporting Information Available:** ORTEP drawings and tables giving fractional atomic coordinates, thermal parameters, and bond distances and angles for **7** and **12c** (12 pages). Ordering information is given on any current masthead page.

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