

## Synthesis and Reactivity of a Dithiolate-Bridged Ruthenium–Rhodium Heterobimetallic Dihydride Complex

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Received October 7, 2005

The new dithiolate-bridged Ru–Rh heterobimetallic dihydride complex [Cp\**Rh*(μ<sub>2</sub>-1,2-S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(μ<sub>2</sub>-H)RuH(PPh<sub>3</sub>)<sub>2</sub>] (**2**) has been prepared, and its reactions with CO and alkynes have been studied. Treatment of the rhodium 1,2-benzenedithiolate complex [Cp\**Rh*(1,2-S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) with [RuHCl(PPh<sub>3</sub>)<sub>3</sub>] in THF produces the hydride- and dithiolate-bridged Ru–Rh heterobimetallic complex [Cp\**Rh*(μ<sub>2</sub>-1,2-S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(μ<sub>2</sub>-H)RuCl(PPh<sub>3</sub>)<sub>2</sub>] (**1**), which was further converted to the dihydride complex [Cp\**Rh*(μ<sub>2</sub>-1,2-S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(μ<sub>2</sub>-H)RuH(PPh<sub>3</sub>)<sub>2</sub>] (**2**) upon treatment with KOH/*i*-PrOH. Complex **2** reacts with CO to give the dicarbonyl complex [Cp\**Rh*(μ<sub>2</sub>-1,2-S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)Ru(CO)<sub>2</sub>(PPh<sub>3</sub>)] (**3**). Reaction of **2** with *p*-tolylacetylene (2 equiv) proceeds with hydrogenation of the alkyne and subsequent oxidative addition of the sp C–H bond to give the alkynyl hydride complex [Cp\**Rh*(μ<sub>2</sub>-1,2-S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(μ<sub>2</sub>-H)Ru(C≡CTol-*p*)(PPh<sub>3</sub>)<sub>2</sub>] (**4a**). The analogous alkynyl hydride complex [Cp\**Rh*(μ<sub>2</sub>-1,2-S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(μ<sub>2</sub>-H)Ru(C≡CSiMe<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (**4b**) has also been prepared. Complex **4a** reacts with excess *p*-tolylacetylene to produce the ruthenacyclopentadiene complex [Cp\**Rh*{μ<sub>2</sub>-η<sup>2</sup>:η<sup>4</sup>-1,3-(*p*-Tol)<sub>2</sub>C<sub>4</sub>H<sub>2</sub>}Ru(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(PPh<sub>3</sub>)] (**5**), whereas similar treatment of **4a** with excess diphenylacetylene induces 1:2 coupling of the two different alkynes to form the η<sup>6</sup>-arene complex [Cp\**Rh*(μ<sub>2</sub>-1,2-S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)Ru{η<sup>6</sup>-C<sub>6</sub>Ph<sub>4</sub>H(*p*-MeC<sub>6</sub>H<sub>4</sub>)}] (**6**). Reaction of **4a** with CO proceeds with dissociation of one of the Ru–S bonds and with retention of the alkynyl hydride structure to give the CO adduct [Cp\**Rh*(μ<sub>2</sub>-1,2-S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(μ<sub>2</sub>-H)Ru(C≡CTol-*p*)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (**7**). The structures of **1**, **3**, **4b**, and **5–7** have been determined by X-ray crystallography.

### Introduction

There continues to be much interest in the chemistry of heterodinuclear transition-metal complexes, in which two different metal atoms are close to each other and thus may behave cooperatively.<sup>1,2</sup> During the last two decades, there have been considerable advances in the methods to synthesize such compounds.<sup>3</sup> In particular, complexes containing terminal thiolate ligands have been recognized as useful building blocks for higher nuclearity compounds.<sup>4–16</sup> Among them, half-

sandwich metal 1,2-dithiolate (or dithiolene) derivatives [(η<sup>5</sup>-Cp')M(S-S)] (Cp' = cyclopentadienyl and substituted cyclopentadienyls; M = Co, Rh, Ir) have attracted much attention.<sup>17–24</sup> Reflecting the coordinatively unsaturated nature of the metal center, these compounds tend to give heteronuclear metal–metal

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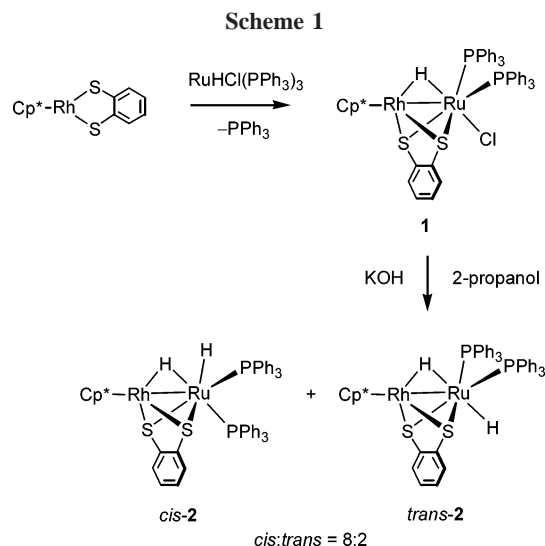
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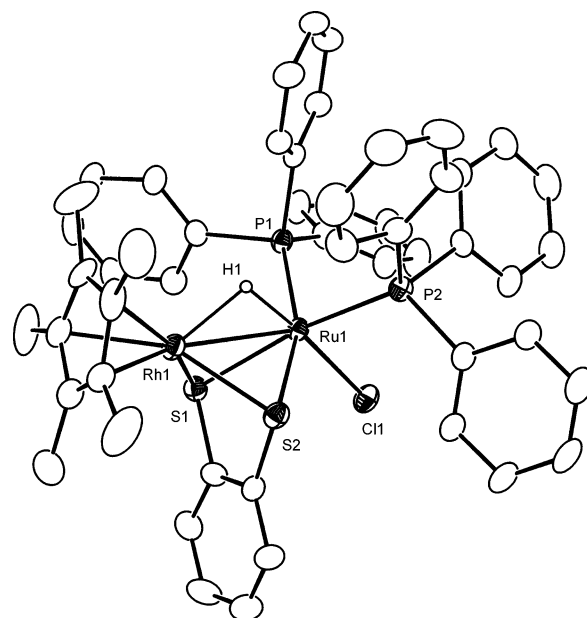
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bonded  $\mu$ -dithiolate compounds upon interaction with Lewis acidic metal fragments.<sup>19,21</sup> As a part of our interest in the chemistry of reactive dinuclear late-transition-metal complexes,<sup>25–28</sup> we have sought to utilize the 16-electron rhodium 1,2-benzenedithiolate complex  $[\text{Cp}^*\text{Rh}(\text{S}_2\text{C}_6\text{H}_4)]^{24}$  for the preparation of heterobimetallic complexes in which the dinuclear core is electronically unsaturated or readily opens up vacant coordination site(s). Herein we report the synthesis of the dithiolate-bridged ruthenium–rhodium heterobimetallic dihydride complex  $[\text{Cp}^*\text{Rh}(\mu\text{-}1,2\text{-S}_2\text{C}_6\text{H}_4)(\mu\text{-H})\text{RuH}(\text{PPh}_3)_2]$  (**2**), which is, to our knowledge, the first example of a thiolate-bridged heterobimetallic dihydride complex. Complex **2** exhibits a chemistry resulting from facile hydrogen loss, producing the lower-valent carbonyl adduct  $[\text{Cp}^*\text{Rh}(\mu\text{-}1,2\text{-S}_2\text{C}_6\text{H}_4)\text{Ru}(\text{CO})_2(\text{PPh}_3)]$  (**3**) upon interaction with carbon monoxide and the alkynyl hydride complexes  $[\text{Cp}^*\text{Rh}(\mu\text{-}1,2\text{-S}_2\text{C}_6\text{H}_4)(\mu\text{-H})\text{Ru}(\text{C}\equiv\text{CR})(\text{PPh}_3)_2]$  (**4a**, R = *p*-Tol; **4b**, R = SiMe<sub>3</sub>) via alkyne C–H bond activation. The reactivity of **4a** toward alkynes and CO is also described.

## Results and Discussion

As outlined in Scheme 1, the hydride- and dithiolate-bridged heterodinuclear framework was readily synthesized by treating the rhodium dithiolate complex  $[\text{Cp}^*\text{Rh}(\text{S}_2\text{C}_6\text{H}_4)]$  with the ruthenium hydride complex  $[\text{RuHCl}(\text{PPh}_3)_3]$  in THF at room temperature. The synthetic strategy is related to that employed for the synthesis of the chloro-bridged heterodinuclear compound  $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})_3\text{RuCl}(\text{PPh}_3)_2]$ .<sup>29</sup> The product  $[\text{Cp}^*\text{Rh}(\mu\text{-}1,2\text{-S}_2\text{C}_6\text{H}_4)(\mu\text{-H})\text{RuCl}(\text{PPh}_3)_2]$  (**1**) was isolated in 84% yield as deep blue plates and characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. The <sup>1</sup>H NMR spectrum is consistent with the bridging hydride formulation, showing a characteristic high-field resonance at  $\delta$  –17.05 (dt, <sup>1</sup>*J*<sub>Rh–H</sub> = 25.7 Hz, <sup>2</sup>*J*<sub>P–H</sub> = 12.8 Hz). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum indicates the existence of chemically equivalent



**Figure 1.** Thermal ellipsoid plot (25% probability level) of  $[\text{Cp}^*\text{Rh}(\mu\text{-}1,2\text{-S}_2\text{C}_6\text{H}_4)(\mu\text{-H})\text{RuCl}(\text{PPh}_3)_2]$  (**1**). Hydrogen atoms, except for the bridging hydride, are omitted for clarity. Selected bond lengths (Å): Rh(1)–Ru(1), 2.7586(7); Rh(1)–S(1), 2.3354(17); Rh(1)–S(2), 2.3540(17); Ru(1)–S(1), 2.4367(17); Ru(1)–S(2), 2.4273(18); Ru(1)–Cl(1), 2.4272(14); Ru(1)–P(1), 2.3089(16); Ru(1)–P(2), 2.3289(17).

triphenylphosphine ligands on ruthenium. An ORTEP drawing of **1** is depicted in Figure 1. The hydride ligand was located in the final difference Fourier map. The molecule contains a triply bridged heterodinuclear core with an intermetallic separation of 2.7586(7) Å, a distance consistent with a Rh–H–Ru three-center–two-electron bond.<sup>30</sup> The rhodium center is coordinated in a three-legged piano-stool geometry, while the ruthenium center is in a distorted-octahedral geometry, in which the terminal chloride ligand is *trans* to the bridging hydride.

Treatment of **1** with excess KOH in 2-propanol at 60 °C afforded the dihydride complex  $[\text{Cp}^*\text{Rh}(\mu\text{-}1,2\text{-S}_2\text{C}_6\text{H}_4)(\mu\text{-H})\text{RuH}(\text{PPh}_3)_2]$  (**2**) (Scheme 1), which was obtained as a mixture of *cis*- and *trans*-dihydride isomers in an 8:2 molar ratio as judged by the <sup>1</sup>H NMR spectrum. Complex **2** was isolated in ~70% yield as an air-sensitive purple microcrystalline solid and characterized by elemental analysis and NMR spectroscopy. Each of the isomers exhibits a set of two distinct hydride resonances in the <sup>1</sup>H NMR spectrum: the *cis* isomer at  $\delta$  –9.79 and –14.00 and the *trans* isomer at  $\delta$  –8.23 and –8.53. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows two mutually coupled doublets ( $\delta$  68.8 and 64.5, <sup>2</sup>*J*<sub>PP</sub> = 11 Hz) attributable to the two inequivalent phosphorus atoms in the *cis* isomer and a singlet resonance at  $\delta$  70.3 for the *trans* isomer.

Di- and polyhydride complexes are frequent sources of lower valent coordinatively unsaturated metal species by undergoing H<sub>2</sub> reductive elimination or transferring dihydrogen to unsaturated substrates.<sup>31</sup> Although the dihydride **2** is thermally stable up to 110 °C in toluene, it reacts smoothly with 2 equiv of carbon monoxide at room temperature to produce the dicarbonyl

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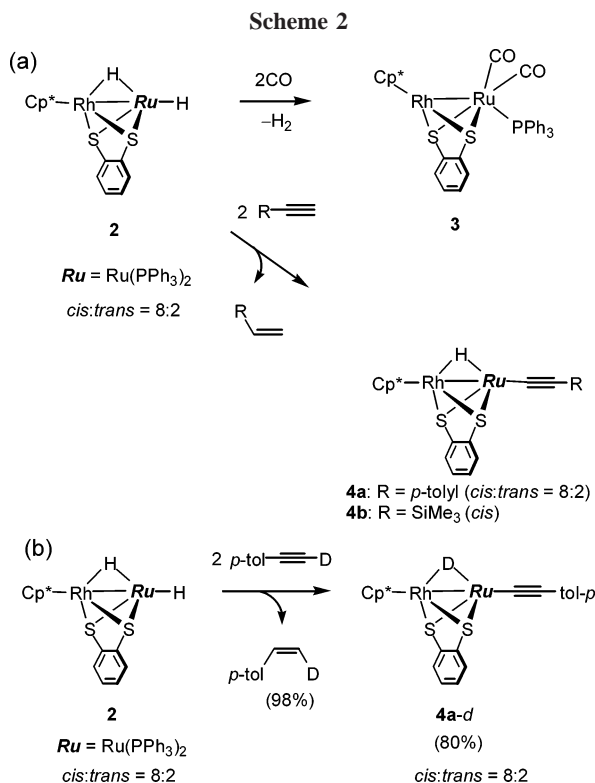
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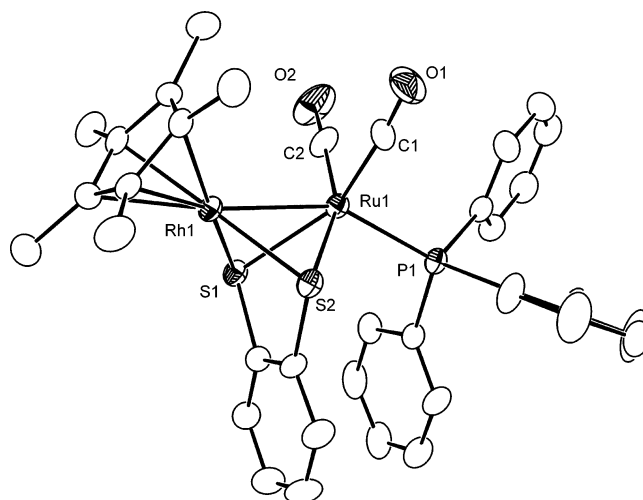
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complex  $[Cp^*Rh(\mu_2-1,2-S_2C_6H_4)Ru(PPh_3)(CO)_2]$  (**3**) (Scheme 2a), which was isolated in 80% yield and characterized by spectroscopic, analytical, and crystallographic methods. Molecular hydrogen was detected by the  $^1H$  NMR spectrum of the reaction mixture, although the amount of the evolved hydrogen was not quantified. We believe coordination of CO induces reductive elimination of  $H_2$  from the dinuclear core. The IR spectrum of **3** shows two  $\nu(CO)$  bands at 1985 and 1921  $cm^{-1}$ , which are comparable to those observed for the bis-thiolate-bridged dimeric ruthenium(I) carbonyl phosphine complexes  $[[Ru(CO)_2(PPh_3)(\mu_2-SR)]_2$ .<sup>32</sup> The  $^{31}P\{^1H\}$  NMR spectrum of **3** displays a doublet resonance at  $\delta$  31.8 ( $^2J_{RhP} = 5.6$  Hz). The observation of Rh–P coupling indicates the existence of a metal–metal single bond between ruthenium and rhodium. The structure of **3** is shown in Figure 2. The molecule contains two five-coordinate metal atoms; the geometry around rhodium is a two-legged piano stool, while that around ruthenium is a distorted square pyramid in which the triphenylphosphine is occupying the apical position. The Ru(1)–Rh(1) distance of 2.61329(12) Å is consistent with a single bond between the two d<sup>7</sup> metal centers,<sup>32,33</sup> which was also indicated by the  $^{31}P\{^1H\}$  NMR spectrum (vide infra).

The dihydride complex **2** reacts with excess *p*-tolylacetylene at room temperature to afford the corresponding alkyne hydride complex  $[Cp^*Rh(\mu_2-1,2-S_2C_6H_4)(\mu_2-H)Ru(C\equiv CTol-p)(PPh_3)_2]$  (**4a**), which was formed as a mixture of *cis* and *trans* isomers (8:2), isolated as cherry red microcrystalline solids, and characterized by analytical and spectroscopic methods. The IR spectrum of **4a** exhibits a  $\nu(C\equiv C)$  band at 2071  $cm^{-1}$ , and the  $^1H$  NMR spectrum shows characteristic high-field resonances



**Figure 2.** Thermal ellipsoid plot (25% probability level) of  $[Cp^*Rh(\mu_2-1,2-S_2C_6H_4)Ru(CO)_2PPh_3]$  (**3**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Rh(1)–Ru(1), 2.6139(12); Rh(1)–S(1), 2.352(2); Rh(1)–S(2), 2.3401(17); Ru(1)–S(1), 2.4299(17); Ru(1)–S(2), 2.4285(18); Ru(1)–C(1), 1.852(7); Ru(1)–C(2), 1.858(7); Ru(1)–P(1), 2.364(2); C(1)–O(1), 1.161(7); C(2)–O(2), 1.143(7).

at  $\delta$  –9.65 (ddd, *cis*) and –10.88 (dt, *trans*) assignable to the bridging hydride. Treatment of **2** with (trimethylsilyl)acetylene afforded the analogous alkyne hydride complex  $[Cp^*Rh(\mu_2-1,2-S_2C_6H_4)(\mu_2-H)Ru(C\equiv CSiMe_3)(PPh_3)_2]$  (**4b**), which was isolated as a single *cis* isomer after recrystallization from toluene–acetonitrile and has been structurally characterized.<sup>34</sup> The structure of **4b** is shown in Figure 3. The Ru(1)–C(1) and C(1)–C(2) bond lengths (2.004(6) and 1.221(10) Å, respectively) as well as Ru(1)–C(1)–C(2) bond angle (169.6(6)°) are typical for Ru(II) terminal alkyne complexes.<sup>35</sup> The Ru(1)–Rh(1) distance of 2.7708(7) Å is comparable to that of **1** and is consistent with the Rh–H–Ru three-center–two-electron bond.

To gain insight into the mechanism of the above alkyne activation, the dihydride complex **2** was treated with 2 equiv of  $DC\equiv CTol-p$  in  $C_6D_6$  in a sealed NMR tube. The  $^1H$  NMR spectrum showed formation of the alkyne deuteride complex  $[Cp^*Rh(\mu_2-1,2-S_2C_6H_4)(\mu_2-D)Ru(C\equiv CTol-p)(PPh_3)_2]$  (**4a-d**) (80%) and the alkene (*Z*)-*p*-TolCH=CHD (98%) (Scheme 2b). This indicates a mechanism involving hydrogen transfer from **2** to the alkyne followed by oxidative addition of a second equivalent of the alkyne to the dinuclear core of the low-valent species “ $Cp^*Rh(\mu_2-1,2-S_2C_6H_4)Ru(PPh_3)_2$ ”. Oxidative addition of alkyne C–H bonds has been observed in several low-valent transition-metal systems.<sup>36,37</sup> The resulting alkyne hydride products are not very stable and often rearrange into vinylidene tautomers.<sup>37</sup> In multimetallic systems, on the other hand, alkyne hydride structures tend to be stable, since both the hydride and

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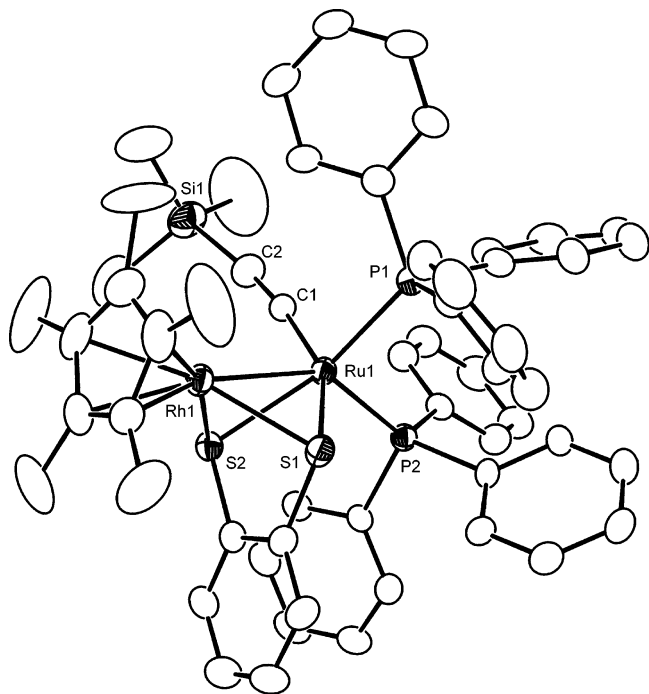
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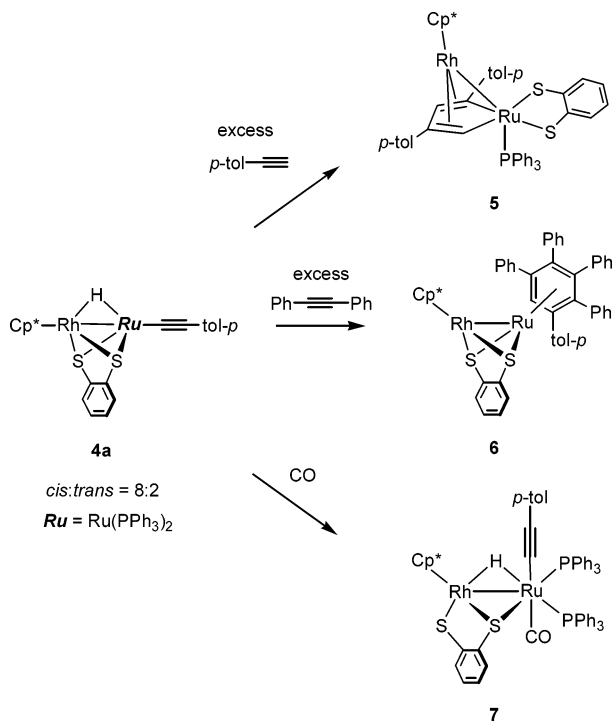
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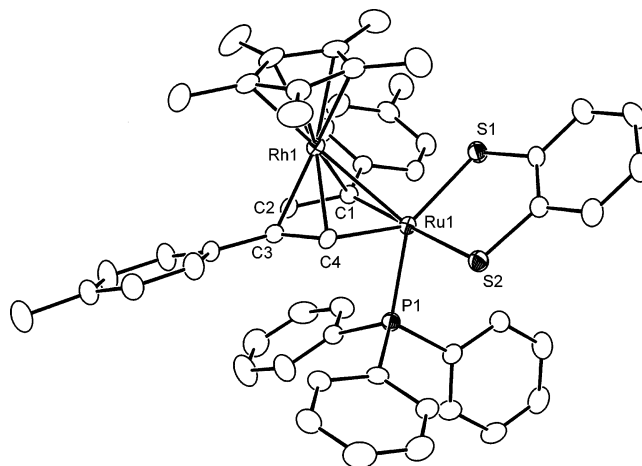
**Figure 3.** Thermal ellipsoid plot (25% probability level) of  $[\text{Cp}^*\text{Rh}(\mu_2\text{-}1,2\text{-S}_2\text{C}_6\text{H}_4)(\mu_2\text{-H})\text{Ru}(\text{C}\equiv\text{CSiMe}_3)(\text{PPh}_3)_2]$  (**4b**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh(1)–Ru(1), 2.7708(7); Rh(1)–S(1), 2.3785(16); Rh(1)–S(2), 2.3587(18); Ru(1)–S(1), 2.4886(17); Ru(1)–S(2), 2.4275(16); Ru(1)–C(1), 2.004(6); Ru(1)–P(1), 2.3070(16); Ru(1)–P(2), 2.3233(16); C(1)–C(2), 1.221(10); C(2)–Si(1), 1.806(8); Ru(1)–C(1)–C(2), 169.6(6); C(1)–C(2)–Si(1), 171.0(7).

## Scheme 3



alkynyl moieties can be stabilized by bridging coordination.<sup>38</sup> The present reaction represents a rare example of dinuclear oxidative addition of alkyne that produces terminal alkynyl moieties.<sup>38b,c</sup>

The alkynyl hydride complex **4a** further reacts with substrates, including alkynes and CO (Scheme 3). Treatment of **4a** with

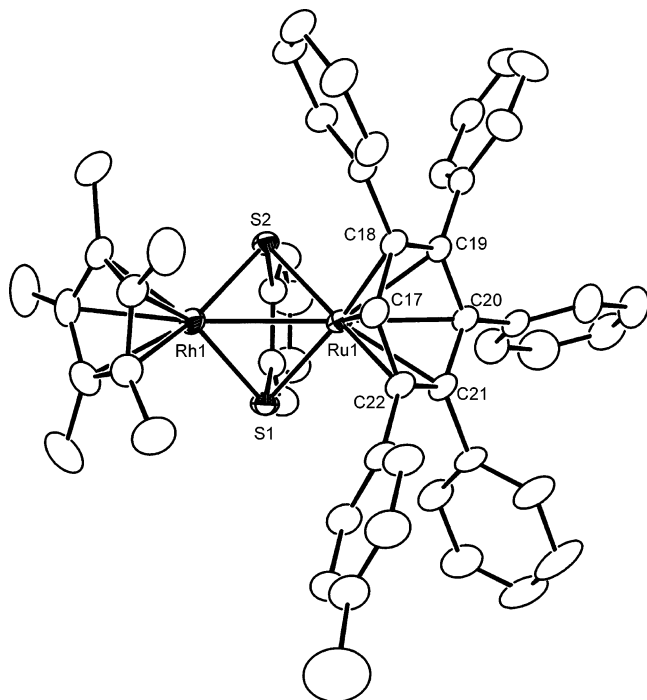


**Figure 4.** Thermal ellipsoid plot (25% probability level) of  $[\text{Cp}^*\text{Rh}(\mu_2\text{-}\eta^4:\eta^2\text{-}1,3\text{-}(p\text{-Tol})_2\text{C}_4\text{H}_2)\text{Ru}(\text{S}_2\text{C}_6\text{H}_4)(\text{PPh}_3)]$  (**5**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Rh(1)–Ru(1), 2.7084(8); Rh(1)–C(1), 2.219(5); Rh(1)–C(2), 2.152(5); Rh(1)–C(3), 2.160(5); Rh(1)–C(4), 2.128(5); Ru(1)–S(1), 2.3039(15); Ru(1)–S(2), 2.3267(14); Ru(1)–P(1), 2.2983(16); Ru(1)–C(1), 2.074(5); Ru(1)–C(4), 1.978(5); C(1)–C(2), 1.420(7); C(2)–C(3), 1.439(7); C(3)–C(4), 1.416(6).

excess of *p*-tolylacetylene in THF at 60 °C afforded the metallocyclopentadiene complex **5**, which is most likely formed via C–H reductive elimination to form a  $\pi$ -alkyne complex, followed by its coupling with another 1 equiv of the alkyne. The reaction is highly selective, and no other metal-containing product was detected in the <sup>1</sup>H NMR spectrum of the crude reaction mixture. After chromatographic workup and recrystallization, complex **5** was isolated in 10% yield<sup>39</sup> as red needles and characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. As shown in Figure 4, the molecule contains an almost planar ruthenacyclopentadiene moiety, which is capped by a {Cp\*Rh} fragment. The C–C bond lengths within the ruthenacyclopentadiene framework are nearly constant (1.416–1.439 Å). The Rh–Ru distance of 2.7084(8) Å indicates a metal–metal bonding interaction, which may be attributed to a dative bond from the 18-electron Rh(I) to 14-electron Ru(IV) centers. The 1,2-benzenedithiolate ligand on ruthenium is terminally bound. The Ru–S bond lengths are 2.2983(16) and 2.3039(15) Å, which are shorter by ~0.1 Å as compared to those observed for 18-electron ruthenium terminal thiolate complexes<sup>23</sup> and suggest a multiple-bond character between ruthenium and sulfur atoms. The solution NMR data are consistent with the solid-state structure. The <sup>1</sup>H NMR spectrum of **5** exhibits characteristic resonances assignable to the metallocyclopentadiene  $\alpha$ - and  $\beta$ -protons at  $\delta$  9.65 (m) and 5.50 (m), respectively. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **5** exhibits four pseudo-triplet resonances at  $\delta$  177.1 ( $^1J_{\text{RhC}} \approx ^2J_{\text{PC}} \approx 16.6$  Hz), 149.5 ( $^1J_{\text{RhC}} \approx ^2J_{\text{PC}} \approx 17.6$  Hz), 115.4 ( $^1J_{\text{RhC}} \approx ^2J_{\text{PC}} \approx 7.4$  Hz), and 95.9 ( $^1J_{\text{RhC}} \approx ^2J_{\text{PC}} \approx 5.2$  Hz), of which the first two can be assigned to the metallocyclopentadiene  $\alpha$ -carbons and the last two to the  $\beta$ -carbons. These <sup>13</sup>C NMR shifts are analogous to those observed for other dinuclear metallacy-

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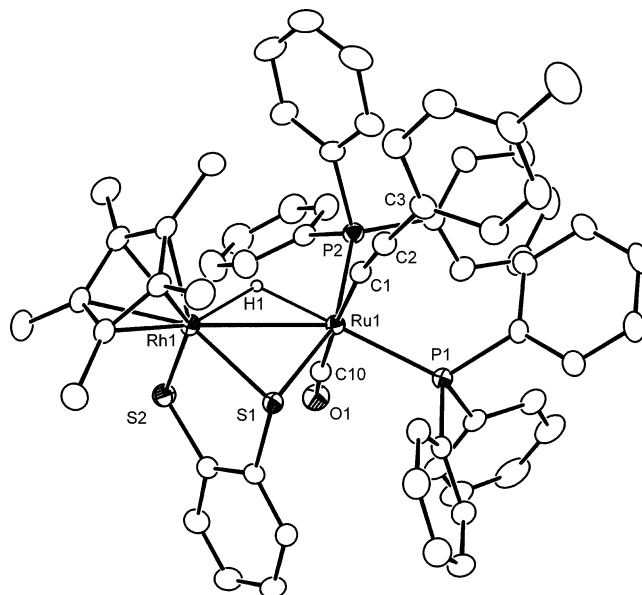
(39) The low isolated yield is due to difficulty in separating **5** from PPh<sub>3</sub>.



**Figure 5.** Thermal ellipsoid plot (25% probability level) of  $[\text{Cp}^*\text{Rh}(\eta^2\text{-}1,2\text{-S}_2\text{C}_6\text{H}_4)\text{Ru}(\eta^6\text{-C}_6\text{Ph}_4\text{H}(p\text{-Tol}))]$  (**6**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Rh(1)–Ru(1), 2.6151(5); Rh(1)–S(1), 2.3061(10); Rh(1)–S(2), 2.3224(9); Ru(1)–S(1), 2.3612(11); Ru(1)–S(2), 2.3654(10); Ru(1)–C(17), 2.190(4); Ru(1)–C(18), 2.196(4); Ru(1)–C(19), 2.191(4); Ru(1)–C(20), 2.246(4); Ru(1)–C(21), 2.204(4); Ru(1)–C(22), 2.239(4).

clopentaadiene complexes<sup>40</sup> and are shifted upfield as compared to those of mononuclear ones.<sup>41</sup> Treatment of **4a** with excess diphenylacetylene led to 1:2 coupling of *p*-tolylacetylene and diphenylacetylene to form the  $\eta^6$ -arene complex **6** (Scheme 3), which was also isolated in 39% yield after chromatography on silica gel, and structurally characterized. The structure of **6** is shown in Figure 5. The two isoelectronic metal fragments  $\{\text{Cp}^*\text{Rh}\}^+$  and  $\{\eta^6\text{-areneRu}\}^+$  are linked together by the bridging  $[\text{S}_2\text{C}_6\text{H}_4]^{2-}$  ligand, and the short metal–metal distance (2.6151(5) Å) is consistent with a metal–metal single bond. Cyclotrimerization of alkynes on transition-metal centers is believed to proceed via oxidative coupling of two  $\pi$ -alkyne ligands followed by insertion of a third alkyne molecule into metal–carbon bonds of the resulting metallacycle.<sup>42</sup> Formation of the metallacyclopentadiene complex **5** and the  $\eta^6$ -arene complex **6** demonstrates the feasibility of alkyne reductive elimination from the alkynyl hydride complex **4a**.

In contrast to the reaction of **4a** with alkynes described above, which induced C–H reductive elimination, treatment of **4a** with carbon monoxide led to incorporation of CO with retention of the alkynyl hydride structure to afford the adduct **7** (Scheme 3). Complex **7** was obtained as a single stereoisomer (by <sup>1</sup>H NMR), isolated in 76% yield as reddish purple plates, and characterized by NMR and IR spectroscopy as well as X-ray



**Figure 6.** Thermal ellipsoid plot (25% probability level) of  $[\text{Cp}^*\text{Rh}(\mu_2\text{-H})(\mu_2\text{-}1,2\text{-S}_2\text{C}_6\text{H}_4)\text{Ru}(\text{C}\equiv\text{CTol-}p)(\text{CO})(\text{PPh}_3)_2]$  (**7**). Hydrogen atoms, except for the bridging hydride, are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh(1)–Ru(1), 2.9467(3); Rh(1)–S(1), 2.2844(7); Rh(1)–S(2), 2.3306(7); Ru(1)–S(1), 2.3974(7); Ru(1)–P(1), 2.3873(7); Ru(1)–P(2), 2.3563(7); Ru(1)–C(1), 2.074(3); Ru(1)–C(10), 1.898(3); C(1)–C(2), 1.208(4); C(10)–O(1), 1.154(3); Ru(1)–C(1)–C(2), 171.7(2); C(1)–C(2)–C(3), 172.2(3).

crystallography. The IR spectrum of **7** exhibits  $\nu(\text{C}\equiv\text{C})$  and  $\nu(\text{CO})$  bands at 2085 and 1967  $\text{cm}^{-1}$ , respectively. The <sup>1</sup>H NMR spectrum of **7** shows a resonance at  $\delta$  –14.84 (ddd, 1H, <sup>1</sup>J<sub>RhH</sub> = 26.6 Hz, <sup>2</sup>J<sub>PH</sub> = 26.6, 16.5 Hz) assignable to the bridging hydride. The structure of **7** is shown in Figure 6. The hydride ligand was found in the difference Fourier map. The two metal centers are doubly bridged by a hydrogen and one of the dithiolate sulfur atoms. Another thiolate moiety is terminally bound to the rhodium center. The carbonyl and alkynyl ligands are coordinated on ruthenium and are mutually trans to each other. The Ru–Rh distance (2.9467(3) Å) is ca. 0.15 Å longer than those of **1** and **4b**, indicating the weakness of the bonding interaction between the two metal centers.

## Conclusions

The interaction between the rhodium dithiolate complex  $[\text{Cp}^*\text{Rh}(\text{S}_2\text{C}_6\text{H}_4)]$  and the ruthenium hydride complex  $[\text{RuHCl}(\text{PPh}_3)_3]$  has been shown to be a straightforward route for the new hydride- and dithiolate-bridged Ru–Rh heterobimetallic complex **1**, which was subsequently converted to the dihydride complex **2**. Complex **2** exhibited further chemistry resulting from facile hydrogen loss, either by reductive elimination or by transfer dehydrogenation. Thus, treatment of **2** with CO induced reductive elimination of H<sub>2</sub> to afford the lower-valent carbonyl adduct **3**, whereas the reaction of **2** with 1-alkynes proceeded via transfer dehydrogenation of **2** followed by oxidative addition of the alkynes to give the alkynyl hydride complexes **4**. The alkynyl hydride complex **4a** has been shown to incorporate carbon monoxide with retention of the alkynyl hydride formulation, whereas it undergoes alkyne reductive elimination and metallacycle formation upon heating with excess alkynes. With these fundamental reactivities in hand, we are currently exploiting the catalytic application of this heterodinuclear system.

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## Experimental Section

All manipulations were carried out using standard Schlenk techniques under an atmosphere of nitrogen. Toluene, hexanes, THF, and diethyl ether were distilled from sodium benzophenone ketyl and degassed before use. Methanol and 2-propanol were distilled from magnesium methoxide or calcium sulfate, respectively, and degassed before use. Acetonitrile was distilled from P<sub>2</sub>O<sub>5</sub> and degassed before use. Deuterated solvents were degassed by three freeze–pump–thaw cycles and stored over 4A molecular sieves. Cp\*Rh(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) and RuHCl(PPh<sub>3</sub>)<sub>3</sub>(toluene) were prepared according to the literature.<sup>24,43</sup> Other chemicals were obtained from commercial sources.

NMR spectra were recorded on a JEOL ECP500 NMR spectrometer operating at 500.16 (<sup>1</sup>H), 202.48 (<sup>31</sup>P), and 125.78 (<sup>13</sup>C) MHz; chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane or 85% phosphoric acid. IR spectra were recorded on a JASCO FT-IR spectrometer. Elemental analyses were performed on a Perkin-Elmer CHNS series II microanalyzer. Mass spectra were measured on a JEOL JMS-700 spectrometer.

**Preparation of [Cp\*Rh(μ<sub>2</sub>-1,2-S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(μ<sub>2</sub>-H)RuCl(PPh<sub>3</sub>)<sub>2</sub>] (1).** To a stirred suspension of Cp\*Rh(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (90 mg, 0.24 mmol) in THF (50 mL) was added RuHCl(PPh<sub>3</sub>)<sub>3</sub>(toluene) (250 mg, 0.246 mmol), and the mixture was stirred overnight at room temperature to form a deep blue solution. Concentration of the solution to ca. 10 mL followed by slow diffusion of diethyl ether (30 mL) afforded deep blue plates, which were collected by filtration and dried in vacuo: yield 210 mg (84%). Anal. Calcd for C<sub>52</sub>H<sub>50</sub>ClP<sub>2</sub>S<sub>2</sub>RuRh: C, 60.03; H, 4.84. Found: C, 60.24; H, 4.96. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.22 (m, 12H, Ph), 7.17 (m, 6H, Ph), 7.11 (m, 2H, S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 7.03 (m, 12H, Ph), 6.60 (m, 2H, S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 1.65 (s, 15H, Cp\*), –17.05 (dt, 1H, <sup>1</sup>J<sub>RhH</sub> = 25.7 Hz, <sup>2</sup>J<sub>PH</sub> = 12.8 Hz, μ<sub>2</sub>-H). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 50.07 (s). MS (FAB): *m/z* 1039 [M – H]<sup>+</sup>.

**Preparation of [Cp\*Rh(μ<sub>2</sub>-1,2-S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(μ<sub>2</sub>-H)RuH(PPh<sub>3</sub>)<sub>2</sub>] (2).** A mixture of **1** (192 mg, 0.185 mmol) and KOH (103 mg, 1.84 mmol) in 2-propanol (20 mL) was stirred at 60 °C for 90 min. The color changed from blue to red. Volatiles were removed in vacuo, and the residue was extracted with toluene (30 mL). Concentration of the extract to ca. 10 mL followed by slow diffusion of methanol (30 mL) afforded a reddish purple microcrystalline solid, which was collected by filtration and dried in vacuo: yield 134 mg (72%). The product was obtained as an 8:2 mixture of *cis* and *trans* isomers. Anal. Calcd for C<sub>52</sub>H<sub>51</sub>P<sub>2</sub>S<sub>2</sub>RuRh: C, 62.08; H, 5.11. Found: C, 62.11; H, 5.38. <sup>1</sup>H NMR for *cis*-**2** (C<sub>6</sub>D<sub>6</sub>): δ 7.78–6.38 (m, 34H, aryl), 1.50 (s, 15H, Cp\*), –9.79, –14.00 (m, 1H each, μ<sub>2</sub>-H and RuH). <sup>31</sup>P{<sup>1</sup>H} NMR for *cis*-**2** (C<sub>6</sub>D<sub>6</sub>): δ 68.8, 65.4 (d, <sup>2</sup>J<sub>PP</sub> = 11.3 Hz). <sup>1</sup>H NMR for *trans*-**2** (C<sub>6</sub>D<sub>6</sub>): δ 7.78–6.38 (m, aryl, overlapped with the aryl resonances of *cis*-**2**), 1.64 (s, 15H, Cp\*), –8.23, –8.53 (m, 1H each, μ<sub>2</sub>-H and RuH). <sup>31</sup>P{<sup>1</sup>H} NMR for *trans*-**2** (C<sub>6</sub>D<sub>6</sub>): δ 70.3 (s). MS (FAB): *m/z* 1005 [M – H]<sup>+</sup>.

**Preparation of [Cp\*Rh(μ<sub>2</sub>-1,2-S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)Ru(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (3).** To a solution of **2** (200 mg, 0.199 mmol) in THF (10 mL) was added carbon monoxide (9 mL, ca. 2 equiv), and the mixture was stirred at room temperature for 4 h. The color changed from red to brown. Volatiles were removed in vacuo, and the residue was recrystallized from toluene–methanol (2 mL/10 mL) to afford dark red plates, which were collected by filtration and dried in vacuo: yield 127 mg (80%). Anal. Calcd for C<sub>36</sub>H<sub>34</sub>O<sub>2</sub>PS<sub>2</sub>RuRh: C, 54.20; H, 4.30. Found: C, 53.58; H, 3.95. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.68 (m, 6H, Ph), 7.01 (m, 9H, Ph), 6.80 (m, 2H, S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 6.03 (m, 2H, S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 2.03 (s, 15H, Cp\*). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 206.2 (dd, <sup>2</sup>J<sub>RhC</sub> = 2.9 Hz, <sup>2</sup>J<sub>PC</sub> = 2.9 Hz, CO), 150.4 (d, <sup>1</sup>J<sub>PC</sub> = 4.8 Hz, aryl), 137.0 (s, aryl), 136.7 (s, aryl), 133.5 (m, aryl), 129.2 (m, aryl), 123.7 (s, aryl), 94.6 (d, <sup>1</sup>J<sub>RhC</sub> = 6.7 Hz, C<sub>5</sub>Me<sub>5</sub>), 11.2 (s, C<sub>5</sub>Me<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H}

NMR (CDCl<sub>3</sub>): δ 31.8 (d, <sup>2</sup>J<sub>RhP</sub> = 5.6 Hz). MS (FAB): *m/z* 798 [M]<sup>+</sup>, 770 [M – CO]<sup>+</sup>, 742 [M – 2CO]<sup>+</sup>. IR (KBr, ν(CO)): 1985, 1921 cm<sup>–1</sup>.

**Preparation of [Cp\*Rh(μ<sub>2</sub>-1,2-S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(μ<sub>2</sub>-H)Ru(C≡CTol-*p*)-(PPh<sub>3</sub>)<sub>2</sub>] (4a).** To a solution of **2** (1.10 g, 1.09 mmol) in THF (100 mL) was added *p*-tolylacetylene (247 mg, 2.13 mmol), and the mixture was stirred at room temperature for 24 h. Concentration of the solution to ca. 10 mL followed by slow diffusion of methanol (30 mL) afforded a reddish purple microcrystalline solid, which was collected by filtration and dried in vacuo: yield 737 mg (60%). The product was obtained as an 8:2 mixture of *cis* and *trans* isomers. Anal. Calcd for C<sub>61</sub>H<sub>57</sub>P<sub>2</sub>S<sub>2</sub>RuRh: C, 65.41; H, 5.13. Found: C, 66.10; H, 5.58. <sup>1</sup>H NMR for *cis*-**4a** (C<sub>6</sub>D<sub>6</sub>): δ 7.8 (m, 12H, Ph), 7.7 (m, 3H, Ph), 7.59 (d, 2H, C<sub>6</sub>H<sub>4</sub>Me), 7.40 (d, 1H, S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 7.11 (d, 2H, C<sub>6</sub>H<sub>4</sub>Me), 7.0 (m, 15H, Ph), 6.29 (d, 1H, S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 6.27 (t, 1H, S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 6.06 (t, 1H, S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 2.24 (s, 3H, C<sub>6</sub>H<sub>4</sub>Me), 1.51 (s, 15H, Cp\*), –9.65 (ddd, 1H, <sup>1</sup>J<sub>RhH</sub> = 26.6 Hz, <sup>2</sup>J<sub>PH</sub> = 26.6, 16.5 Hz, μ<sub>2</sub>-H). <sup>31</sup>P{<sup>1</sup>H} NMR for *cis*-**4a** (C<sub>6</sub>D<sub>6</sub>): δ 52.9, 50.7 (d, <sup>2</sup>J<sub>PP</sub> = 25 Hz). <sup>1</sup>H NMR for *trans*-**2** (C<sub>6</sub>D<sub>6</sub>): δ 7.9–6.0 (m, aryl, overlapped with the aryl resonances of *cis*-**4a**), 2.20 (s, 3H, C<sub>6</sub>H<sub>4</sub>Me), 1.53 (s, 15H, Cp\*), –10.88 (dt, 1H, <sup>1</sup>J<sub>RhH</sub> = 29.3 Hz, <sup>2</sup>J<sub>PH</sub> = 9.2 Hz, μ<sub>2</sub>-H). <sup>31</sup>P{<sup>1</sup>H} NMR for *trans*-**2** (C<sub>6</sub>D<sub>6</sub>): δ 55.1 (s). MS (FAB): *m/z* 1120 [M]<sup>+</sup>. IR (KBr, ν(C≡C)): 2071 cm<sup>–1</sup>.

**Preparation of [Cp\*Rh(μ<sub>2</sub>-1,2-S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(μ<sub>2</sub>-H)Ru(C≡CSiMe<sub>3</sub>)-(PPh<sub>3</sub>)<sub>2</sub>] (4b).** To a solution of **2** (100 mg, 0.0994 mmol) in THF (10 mL) was added (trimethylsilyl)acetylene (19 mg, 0.19 mmol), and the mixture was stirred at room temperature for 19 h. Volatiles were removed in vacuo, and the residue was recrystallized from toluene–acetonitrile (2 mL/10 mL) to afford dark red plates, which were collected by filtration and dried in vacuo: yield 82 mg (75%). Anal. Calcd for C<sub>57</sub>H<sub>59</sub>SiP<sub>2</sub>S<sub>2</sub>RuRh: C, 62.11; H, 5.40. Found: C, 62.02; H, 5.38. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.86–7.05 (m, 30H, Ph), 6.90, 6.24, 6.22, 6.03 (m, 1H each, S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 1.52 (s, 15H, Cp\*), 0.50 (s, 9H, SiMe<sub>3</sub>), –9.76 (ddd, 1H, <sup>1</sup>J<sub>RhH</sub> = 25.7 Hz, <sup>2</sup>J<sub>PH</sub> = 25.7, 16.5 Hz, μ<sub>2</sub>-H). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 52.6, 49.4 (d, <sup>2</sup>J<sub>PP</sub> = 26 Hz). IR (KBr, ν(C≡C)): 1994 cm<sup>–1</sup>.

**Preparation of [Cp\*Rh(μ<sub>2</sub>-η<sup>2</sup>:η<sup>2</sup>-1,3-(*p*-Tol)<sub>2</sub>C<sub>4</sub>H<sub>2</sub>)Ru(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)-(PPh<sub>3</sub>)<sub>3</sub>] (5).** To a solution of **4a** (270 mg, 0.241 mmol) in THF (20 mL) was added *p*-tolylacetylene (156 mg, 1.34 mmol), and the mixture was stirred at 60 °C for 16 h. The solution was concentrated to ca. 2 mL and then loaded onto a short silica gel column (1 cm o.d., 10 cm). Elution with toluene gave a red band, which was collected, concentrated to ca. 2 mL, and then layered with methanol (10 mL). The red needlelike crystals formed were collected by filtration and dried in vacuo: yield 25 mg (10%). The crystals contain one solvating toluene per molecule of **5**. Anal. Calcd for C<sub>52</sub>H<sub>50</sub>PS<sub>2</sub>RuRh·C<sub>7</sub>H<sub>8</sub>: C, 66.47; H, 5.48. Found: C, 67.10; H, 5.74. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.65 (m, 1H, (*p*-Tol)CCHC(*p*-Tol)CH), 8.21 (m, 2H, aryl), 7.7–7.0 (m, 25H, aryl), 5.50 (m, 1H, (*p*-Tol)CCHC(*p*-Tol)CH), 2.35, 2.33 (s, 3H each, C<sub>6</sub>H<sub>4</sub>Me), 1.20 (s, 15H, Cp\*). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 62.4 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 177.1 (pseudo t, <sup>1</sup>J<sub>RhC</sub> ≈ <sup>2</sup>J<sub>PC</sub> ≈ 16.6 Hz, (*p*-Tol)CCHC(*p*-Tol)CH), 149.5 (pseudo t, <sup>1</sup>J<sub>RhC</sub> ≈ <sup>2</sup>J<sub>PC</sub> ≈ 17.6 Hz, (*p*-Tol)CCHC(*p*-Tol)CH), 115.4 (pseudo t, <sup>1</sup>J<sub>RhC</sub> ≈ <sup>3</sup>J<sub>PC</sub> ≈ 7.4 Hz, (*p*-Tol)CCHC(*p*-Tol)CH), 95.9 (pseudo t, <sup>1</sup>J<sub>RhC</sub> ≈ <sup>3</sup>J<sub>PC</sub> ≈ 5.2 Hz, (*p*-Tol)CCHC(*p*-Tol)CH), 159.7, 145.4, 136.8, 136.0, 135.4, 134.9, 134.1, 133.6, 131.4, 130.4, 130.0, 128.8, 128.5, 128.3, 128.0, 127.7, 126.9, 125.5 (s, aryl), 98.2 (d, <sup>1</sup>J<sub>RhC</sub> = 18 Hz, C<sub>5</sub>Me<sub>5</sub>), 21.4, 21.3 (s, C<sub>6</sub>H<sub>4</sub>Me), 9.6 (s, C<sub>5</sub>Me<sub>5</sub>). MS (FAB): *m/z* 974 [M]<sup>+</sup>.

**Preparation of [Cp\*Rh(μ<sub>2</sub>-1,2-S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)Ru(η<sup>6</sup>-C<sub>6</sub>Ph<sub>4</sub>H(*p*-Tol))] (6).** To a solution of **4a** (200 mg, 0.179 mmol) in THF (20 mL) was added diphenylacetylene (159 mg, 0.893 mmol), and the mixture was stirred at 60 °C for 16 h. The mixture was concentrated to ca. 2 mL and then loaded onto a short silica gel column (1 cm o.d., 10 cm). Elution with toluene gave a red band, which was collected and evaporated to dryness. Recrystallization of the residue from THF–methanol (3 mL/12 mL) afforded red blocks, which

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**Table 1.** Crystallographic Data for **1**, **3**, **4b**, **5**·(toluene), **6**, and **7**

	<b>1</b>	<b>3</b>	<b>4b</b>	<b>5</b> ·(toluene)	<b>6</b>	<b>7</b>
formula	C <sub>52</sub> H <sub>50</sub> ClP <sub>2</sub> S <sub>2</sub> - RuRh	C <sub>36</sub> H <sub>34</sub> O <sub>2</sub> PS <sub>2</sub> - RuRh	C <sub>57</sub> H <sub>59</sub> SiP <sub>2</sub> S <sub>2</sub> - RuRh	C <sub>59</sub> H <sub>58</sub> PS <sub>2</sub> - RuRh	C <sub>33</sub> H <sub>47</sub> S <sub>2</sub> RuRh	C <sub>62</sub> H <sub>57</sub> OP <sub>2</sub> S <sub>2</sub> - RuRh
<i>M<sub>r</sub></i>	1040.41	797.70	1102.17	1066.12	952.01	1148.12
<i>T</i> (K)	296	296	296	296	296	296
size (mm)	0.80 × 0.30 × 0.01	0.50 × 0.15 × 0.01	0.70 × 0.60 × 0.30	0.50 × 0.10 × 0.10	0.50 × 0.40 × 0.30	0.60 × 0.20 × 0.10
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>Pca</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>Z</i>	4	4	4	4	2	4
<i>a</i> (Å)	19.5760(16)	12.401(9)	13.1118(12)	11.042(3)	13.4280(14)	12.0433(6)
<i>b</i> (Å)	12.9958(17)	22.984(12)	21.503(3)	28.500(8)	13.4077(17)	23.0234(11)
<i>c</i> (Å)	18.3713(16)	13.023(6)	19.348(2)	15.871(5)	13.450(2)	19.3711(12)
$\alpha$ (deg)					95.065(5)	
$\beta$ (deg)		113.77(4)	94.862(5)	92.80(2)	100.779(5)	90.638(3)
$\gamma$ (deg)					108.421(5)	
<i>V</i> (Å <sup>3</sup> )	4673.8(8)	3397(3)	5435.4(10)	4989(2)	2228.4(5)	5370.8(5)
<i>D</i> <sub>calcd</sub> (g/cm <sup>3</sup> )	1.479	1.560	1.347	1.419	1.419	1.420
$\mu$ (mm <sup>-1</sup> )	0.926	1.131	0.774	0.787	0.838	0.767
no. of rflns collected	41 576	32 734	50 617	48 834	21 389	49 209
no. of unique rflns	9983	7766	23 938	11 433	10 103	12 098
GOF on <i>F</i> <sup>2</sup>	1.024	0.930	0.937	1.020	0.966	1.001
R1 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) <sup>a</sup>	0.0498	0.0534	0.0517	0.0713	0.0430	0.0356
wR2 (all data) <sup>b</sup>	0.1170	0.1039	0.1484	0.1181	0.1036	0.0800

<sup>a</sup> R1 =  $\sum||F_o| - |F_c||/\sum|F_o|$ . <sup>b</sup> wR2 =  $[\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$ .

were collected by filtration and dried in vacuo: yield 66 mg (39%). Anal. Calcd for C<sub>53</sub>H<sub>47</sub>S<sub>2</sub>RuRh: C, 66.86; H, 4.98. Found: C, 66.81; H, 5.21. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  8.24–6.54 (m, 29H, aryl), 2.01 (s, 3H, C<sub>6</sub>H<sub>4</sub>Me), 1.61 (s, 15H, Cp\*). MS (FAB): *m/z* 952 [M]<sup>+</sup>.

**Preparation of [Cp\**Rh*( $\mu_2$ -H)( $\mu_2$ -1,2-S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)Ru(C $\equiv$ CTol-*p*)-(CO)(PPh<sub>3</sub>)<sub>2</sub>] (7).** A 20 mL Schlenk flask was charged with **4a** (97 mg, 0.086 mmol) and THF (10 mL). After the solution was frozen at –196 °C, the flask was evacuated, warmed to room temperature, and then filled with atmospheric carbon monoxide. The mixture was stirred at room temperature for 18 h and concentrated in vacuo to ca. 2 mL. Slow diffusion of methanol (30 mL) into the concentrated reaction solution afforded reddish purple plates, which were collected by filtration and dried in vacuo: yield 75 mg (76%). Anal. Calcd for C<sub>62</sub>H<sub>57</sub>OP<sub>2</sub>S<sub>2</sub>RuRh: C, 64.86; H, 5.00. Found: C, 64.19; H, 5.35. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.83 (m, 14H, aryl), 7.12–6.96 (m, 22H, aryl), 6.82, 6.56 (m, 1H each, aryl), 2.16 (s, 3H, C<sub>6</sub>H<sub>4</sub>Me), 1.66 (s, 15H, Cp\*), –14.84 (ddd, 1H, <sup>1</sup>J<sub>RhH</sub> = 26.6 Hz, <sup>2</sup>J<sub>PH</sub> = 26.6, 16.5 Hz,  $\mu_2$ -H). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  41.3, 29.4 (d, <sup>2</sup>J<sub>PP</sub> = 20 Hz). MS (FAB): *m/z* 1148 [M]<sup>+</sup>. IR (KBr):  $\nu$ (C $\equiv$ C) 2085 cm<sup>-1</sup>,  $\nu$ (CO) 1967 cm<sup>-1</sup>.

**X-ray Crystallography.** Reflection data were collected at 296 K with a Rigaku RAXIS Rapid diffractometer equipped with an imaging plate detector. The frame data were processed using the Rigaku PROCESS-AUTO program,<sup>44</sup> and the reflection data were corrected for absorption with the ABSCOR program.<sup>45</sup> The

structures were solved by direct methods and refined on *F*<sup>2</sup> by full-matrix least-squares methods with the SHELX97 program package.<sup>46</sup> Anisotropic refinement was applied to all non-hydrogen atoms. Hydrogen atoms were located at the calculated positions and treated as riding models, except for the hydride ligand in **1**, which was found in the final difference Fourier map and refined isotropically. Crystallographic data are summarized in Table 1.

**Acknowledgment.** Financial support from the Ministry of Education, Science, Sports, and Culture of Japan, including a Grant-in-Aid for Scientific Research on Priority Areas (No. 17036059 “Chemistry of Coordination Space”), is appreciated. We are also grateful to the Toyota Motor Corp. for financial support.

**Supporting Information Available:** Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM050871N

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