

## Novel Early-late Transition Metal Complexes. The First Thiolato Bridged Titanium-Ruthenium Complexes

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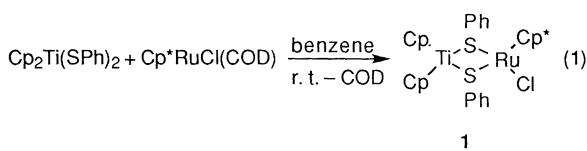
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A series of novel thiolato-bridged titanium-ruthenium mixed metal complexes,  $\text{Cp}_2\text{Ti}(\mu\text{-SPh})_2\text{RuClCp}^*$ ,  $\text{Cp}_2\text{Ti}(\mu\text{-SPh})_2\text{RuHCp}^*$  and  $[\text{Cp}_2\text{Ti}(\mu\text{-SPh})_2\text{Ru}(\text{L})\text{Cp}^*][\text{PF}_6]$  ( $\text{L} = \text{CH}_3\text{CN}, \text{t-BuCN}$ ) are prepared.

Recently, much attention has been paid to early-late heterobimetallics (ELHB)<sup>1</sup> which show characteristic reactivity because they contain d-electron deficient early transition metal and d-electron rich late transition metal in one molecule. To prepare the ELHB complexes, reactions of metalloligand  $[\text{Cp}_2\text{M}(\text{SR})_2]$  ( $\text{Cp} = \text{cyclopentadienyl}$ ,  $\text{M} = \text{early transition metal}$ ) with late transition metal complexes  $[\text{M}'\text{L}_n]$  have been investigated. In some cases thiolato-bridged  $[\text{Cp}_2\text{M}(\mu\text{-SR})_2\text{M}'\text{L}_n]$  was synthesized<sup>1a-1d</sup>, and in other cases thiolato ligand transfer occurred giving  $\text{M}'(\text{SR})_2(\text{L})_n$ .<sup>1c,2</sup> In this paper we wish to report the synthesis, structure and reactivity of the first thiolato-bridged titanium-ruthenium complexes.

The reaction of  $\text{Cp}_2\text{Ti}(\text{SPh})_2$  with  $\text{Cp}^*\text{RuCl}(\text{COD})$  ( $\text{Cp}^* = \text{pentamethylcyclopentadienyl}$ ) in benzene liberated COD, affording novel thiolato-bridged complex  $\text{Cp}_2\text{Ti}(\mu\text{-SPh})_2\text{RuClCp}^*$  (**1**)<sup>3</sup> in 79% yield (eq 1). This complex is the first example of a thiolato-bridged Ti-Ru complex.



To confirm the structure of **1**, X-ray analysis was performed.<sup>4</sup> The molecular structure of **1** is illustrated in Figure 1. The geometries around the Ti and Ru centers of **1** are described as pseudotetrahedral and three-legged pianostool, respectively. The complex **1** has a four-membered ring of Ti, Ru and two S atoms. The  $\text{TiS}_2\text{Ru}$  core is slightly puckered, with an angle of  $9.11^\circ$  between the  $\text{S1-Ru-S2}$  and the  $\text{S1-Ti-S2}$  planes. Two phenyl rings on the sulfur atoms are in *syn* conformation. The Ti-S distances of  $2.468(5)$  and  $2.464(6)$  Å are somewhat longer than those observed for  $\text{Cp}_2\text{Ti}(\text{SPh})_2$  ( $2.395(8)$ ,  $2.424(8)$  Å).<sup>5</sup> The S-Ti-S angle ( $96.1(2)^\circ$ ) is slightly smaller than that for  $\text{Cp}_2\text{Ti}(\text{SPh})_2$  ( $99.3(3)^\circ$ ).<sup>5</sup>

The  $^1\text{H}$  NMR spectrum of the complex **1** showed resonances for two nonequivalent Cp rings on Ti (5.44 and 5.16 ppm) and two equivalent phenyl groups. No temperature dependence of these resonances in the range 353–298 K was observed. The NMR study and the results of X-ray analysis indicate that two phenyl rings of **1** are in *syn* conformation even in solution. The *syn-anti* interconversion (eq 2) discussed in  $[\text{Cp}_2\text{Ti}(\mu\text{-SEt})_2\text{CuL}][\text{PF}_6]$  [ $\text{L} = \text{PPh}_3, \text{PCy}_3, \text{PEt}_3$  etc.]<sup>1b</sup> and  $[\text{Cp}_2\text{Ti}(\mu\text{-SMe})_2\text{Cu}(\text{NCMe})_2][\text{PF}_6]$ ,<sup>1d</sup> is suppressed probably because of steric hindrance of  $\text{Cp}^*$  ring on Ru.

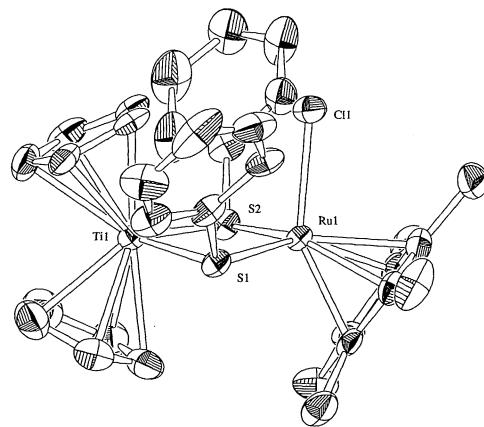
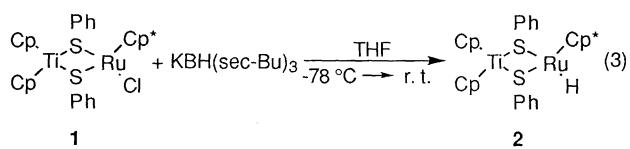
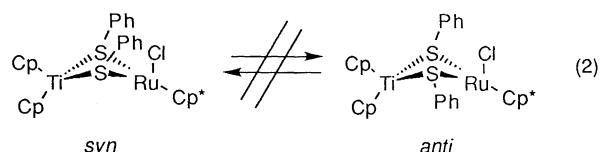


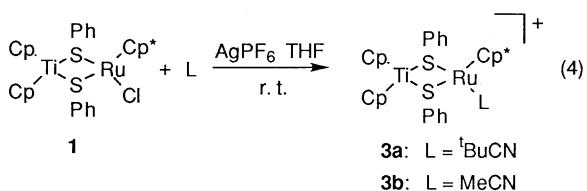
Figure 1. ORTEP drawing of **1** (30% probability thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Ti1-S1 2.468(5), Ti1-S2 2.464(6), Ru1-S1 2.353(5), Ru1-S2 2.338(5), Ru1-Cl1 2.451(5), S1-Ti1-S2 96.1(2), S1-Ru1-S2 102.9(2), Ti1-S1-Ru1 80.0(2), Ti1-S2-Ru1 80.4(2).



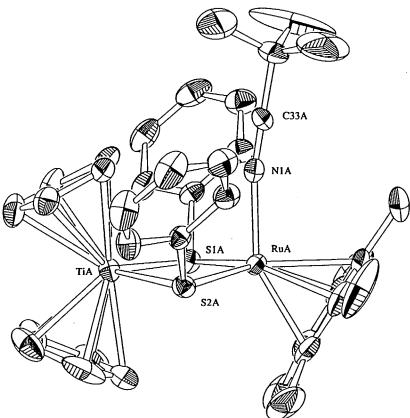
From the complex **1**, a variety of derivative complexes were prepared.

The complex **1** reacted with  $\text{KBH}(\text{sec-Bu})_3$  to give a hydrido complex,  $\text{Cp}_2\text{Ti}(\mu\text{-SPh})_2\text{RuHCp}^*$  (**2**),<sup>6</sup> in 95% yield (eq 3). In the IR spectrum of **2**, an absorption of  $\nu(\text{Ru-H})$  was observed at  $1937 \text{ cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum of **2** showed nonequivalent two Cp resonances at 5.25 and 4.59 ppm, which shifted upfield compared with those of **1**. The signal assigned to the hydride on Ru was observed at  $-14.46 \text{ ppm}$ .

The complex **1** reacted with  $\text{AgPF}_6$  in the presence of ligands L ( $\text{L} = \text{t-BuCN}$  or  $\text{MeCN}$ ) to give thiolato-bridged early-late bimetallic cation complexes  $[\text{Cp}_2\text{Ti}(\mu\text{-SPh})_2\text{RuLCp}^*][\text{PF}_6]$  (**3a, b**)<sup>7</sup> in 76 and 11% yields (eq 4).



To confirm the structure of **3a**, X-ray analysis was performed.<sup>8</sup> In the unit cell there are two independent molecules A and B, which are very similar to each other except for the orientation of the phenyl groups. The structure of cation of **3a** (one of the pair of independent molecules) is illustrated in Figure 2. The structure of the cation of **3a** was principally similar to that of **1**.



**Figure 2.** ORTEP drawing of the cation of **3a** [one of the pair of independent molecules (molecule A), 30% probability thermal ellipsoids]. Selected bond lengths [Å] and angles [°]: TiA-S1A 2.459(3), TiA-S2A 2.463(3), RuA-S1A 2.368(2), RuA-S2A 2.370(2), RuA-N1A 2.047(7), S1A-TiA-S2A 95.91(9), S1A-RuA-S2A 100.96(8), TiA-S1A-RuA 81.17(8), TiA-S2A-RuA 81.05(8), TiB-S1B 2.472(3), TiB-S2B 2.467(3), RuB-S1B 2.362(2), RuB-S2B 2.362(2), RuB-N1B 2.056(7), S1B-TiB-S2B 97.07(9), S1B-RuB-S2B 103.18(8), TiB-S1B-RuB 79.65(7), TiB-S2B-RuB 79.75(8).

The complementary reactivities of the early and late transition metals in **1**, **2** and **3** are expected. Further investigation on reactivities of these complexes is in progress.

#### References and Notes

- 1 a) D. W. Stephan, *Cood. Chem. Rev.*, **95**, 41 (1989). b) T. A. Wark and D. W. Stephan, *Inorg. Chem.*, **26**, 363 (1987). c) T. A. Wark and D. W. Stephan, *Organometallics*, **8**, 2836 (1989). d) T. A. Wark and D. W. Stephan, *Inorg. Chem.*, **29**, 1731 (1990). e) A. M. Baranger and R. G. Bergman, *J. Am. Chem. Soc.*, **116**, 3822 (1994). f) M. A. Aubart and R. G. Bergman, *J. Am. Chem. Soc.*, **118**, 1793 (1996). g) F. Ozawa, J. W. Park, P. B. Mackenzie, W. P. Schaefer, L. M. Henling, and R. H. Grubbs, *J. Am. Chem. Soc.*, **111**, 1319 (1989). h) J. Sundermeyer and D. Runge, *Angew. Chem. Int. Ed. Engl.*, **33**, 1255 (1994). i) S. Friedrich, H. Memmler, L. H. Gade, W. S. Li, I. J. Scowen, M. McPartlin, and C. E. Housecroft, *Inorg. Chem.*, **35**, 2433 (1996).
- 2 K. Osakada, Y. Kawaguchi, and T. Yamamoto, *Organometallics*, **14**, 4542 (1995).
- 3 **1**: brown powder. Mp: 143.0-146.0 °C (decomp). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.90-7.87, 7.29-7.11 (m, 10H, Ph), 5.44 (s, 5H, Cp), 5.16 (s, 5H, Cp), 1.65 (s, 15H, Cp\*). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 143.2 (Ph), 131.8 (Ph), 127.8 (Ph), 125.6 (Ph), 110.4 (Cp), 104.3 (Cp), 91.4 (C<sub>5</sub>Me<sub>5</sub>), 9.9 (C<sub>5</sub>Me<sub>5</sub>). Anal. Found: C, 57.29; H, 5.51; Cl, 5.74%. Calcd for C<sub>32</sub>H<sub>35</sub>ClS<sub>2</sub>RuTi: C, 57.52; H, 5.28; Cl, 5.31%.
- 4 X-ray structure analysis of **1**: C<sub>32</sub>H<sub>35</sub>ClS<sub>2</sub>RuTi, F.W.=668.17, space group *P*2<sub>1</sub>/*n*, Z=4, *a*=12.201(7), *b*=16.718(4), *c*=20.689(4) Å, β=100.34(2)°, V=4151(2) Å<sup>3</sup>, ρ<sub>calcd</sub>=1.069 gcm<sup>-3</sup>. 9921 measured, 9467 independent reflections, of which 1876 were considered as observed [*I*>3.50σ(*I*)]. *R*=0.072, *R*<sub>w</sub>=0.073.
- 5 E. G. Muller, S. F. Watkins, and L. F. Dahl, *J. Organomet. Chem.*, **111**, 73 (1976).
- 6 **2**: brown powder. Mp: 170.0-175.0 °C (decomp). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.75-7.09 (m, 10H, Ph), 5.25 (s, 5H, Cp), 4.59 (s, 5H, Cp), 1.78 (s, 15H, Cp\*), -14.46 (s, 1H, Ru-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 147.0 (Ph), 125.5 (Ph), 107.5 (Cp), 103.8 (Cp), 94.0 (C<sub>5</sub>Me<sub>5</sub>), 10.6 (C<sub>5</sub>Me<sub>5</sub>). IR (KBr): ν(Ru-H), 1937 cm<sup>-1</sup>.
- 7 **3a**: dark violet crystals. Mp: 143.0-146.3 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.44-7.26 (m, 10H, Ph), 5.63 (s, 5H, Cp), 5.07 (s, 5H, Cp), 1.73 (s, 15H, Cp\*), 1.07 (s, 9H, t-Bu). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 141.6 (Ph), 137.4 (CN), 131.0 (Ph), 129.5 (Ph), 127.4 (Ph), 110.8 (Cp), 106.9 (Cp), 93.9 (C<sub>5</sub>Me<sub>5</sub>), 30.9 (Me<sub>3</sub>C), 25.9 (Me<sub>3</sub>C), 10.2 (C<sub>5</sub>Me<sub>5</sub>). Anal. Found: C, 48.15; H, 4.89; N, 1.50%. Calcd for C<sub>37</sub>H<sub>44</sub>F<sub>6</sub>NPS<sub>2</sub>RuTi•CH<sub>2</sub>Cl<sub>2</sub>: C, 48.16; H, 4.89; N, 1.63%. **3b**: dark violet crystals. Mp: 116.0-121.5 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.41-7.26 (m, 10H, Ph), 5.59 (s, 5H, Cp), 4.99 (s, 5H, Cp), 2.03 (s, 3H, MeCN), 1.74 (s, 15H, Cp\*). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 141.4 (Ph), 130.9 (Ph), 129.5 (Ph), 127.9 (CN), 127.4 (Ph), 110.6 (Cp), 106.6 (Cp), 94.2 (C<sub>5</sub>Me<sub>5</sub>), 10.1 (C<sub>5</sub>Me<sub>5</sub>), 4.1 (MeCN). Anal. Found: C, 46.36; H, 4.47; N, 1.57%. Calcd for C<sub>34</sub>H<sub>38</sub>F<sub>6</sub>NPS<sub>2</sub>RuTi•CH<sub>2</sub>Cl<sub>2</sub>: C, 46.52; H, 4.46; N, 1.55%.
- 8 X-ray structure analysis of **3a**: C<sub>37</sub>H<sub>44</sub>F<sub>6</sub>NPS<sub>2</sub>RuTi•CH<sub>2</sub>Cl<sub>2</sub>, F.W.=945.75, space group *P*1, Z=4, *a*=16.567(4), *b*=22.618(7), *c*=11.885(8) Å, α=102.90(5), β=96.37(5), γ=71.20(2)°, V=4105(3) Å<sup>3</sup>, ρ<sub>calcd</sub>=1.510 gcm<sup>-3</sup>. 19519 measured, 18865 independent reflections, of which 7920 were considered as observed [*I*>3.00σ(*I*)]. *R*=0.056, *R*<sub>w</sub>=0.054.