

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

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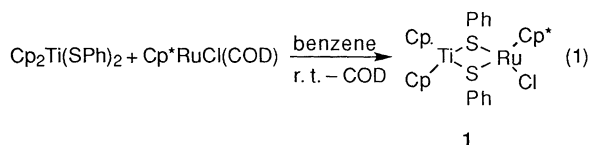
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A series of novel thiolato-bridged titanium-ruthenium mixed metal complexes, $\text{Cp}_2\text{Ti}(\mu\text{-SPh})_2\text{RuClCp}^*$, $\text{Cp}_2\text{Ti}(\mu\text{-SPh})_2\text{RuHCP}^*$ and $[\text{Cp}_2\text{Ti}(\mu\text{-SPh})_2\text{Ru(L)Cp}^*][\text{PF}_6]$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

Recently, much attention has been paid to early-late heterobimetallics (ELHB)¹ 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 $[\text{Cp}_2\text{M}(\text{SR})_2]$ (Cp = cyclopentadienyl, M = 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^{1a-1d}, and in other cases thiolato ligand transfer occurred giving $\text{M}'(\text{SR})_2(\text{L})_n$.^{1c,2} 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 $\text{Cp}^*\text{RuCl}(\text{COD})$ (Cp^* = pentamethylcyclopentadienyl) in benzene liberated COD, affording novel thiolato-bridged complex $\text{Cp}_2\text{Ti}(\mu\text{-SPh})_2\text{RuClCp}^*$ (**1**)³ 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.⁴ 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 TiS_2Ru core is slightly puckered, with an angle of 9.11° between the S1-Ru-S2 and the 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).⁵ The S-Ti-S angle ($96.1(2)^\circ$) is slightly smaller than that for $\text{Cp}_2\text{Ti}(\text{SPh})_2$ ($99.3(3)^\circ$).⁵

The ^1H 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 $[\text{Cp}_2\text{Ti}(\mu\text{-SEt})_2\text{CuL}][\text{PF}_6]$ [$\text{L} = \text{PPh}_3$, PCy_3 , PET_3 etc.]^{1b} and $[\text{Cp}_2\text{Ti}(\mu\text{-SMe})_2\text{Cu}(\text{NCMe})_2][\text{PF}_6]$,^{1d} is suppressed probably because of steric hindrance of Cp^* ring on Ru.

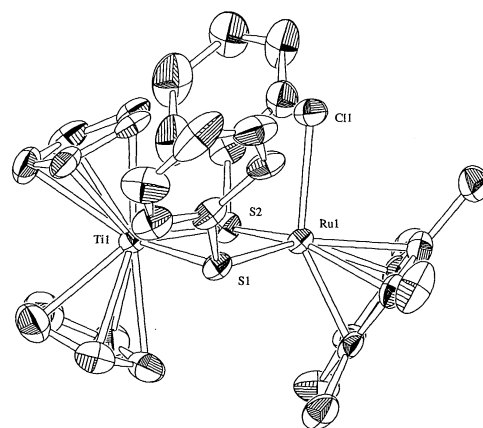
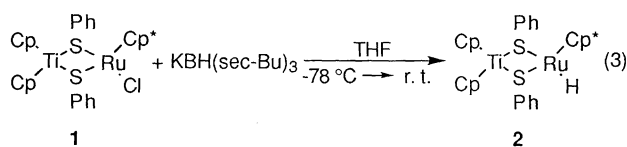
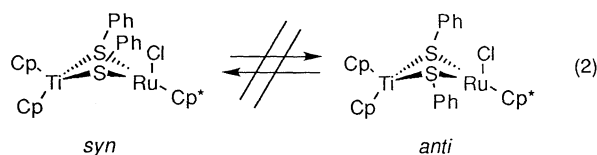


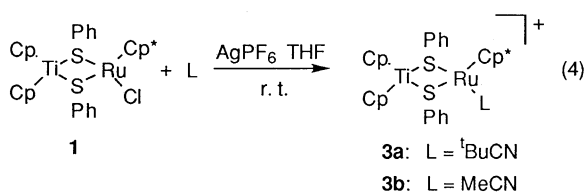
Figure 1. ORTEP drawing of **1** (30% probability thermal ellipsoids). Selected bond lengths [Å] and angles [$^\circ$]: Ti-S1 2.468(5), Ti-S2 2.464(6), Ru-S1 2.353(5), Ru-S2 2.338(5), Ru-Cl1 2.451(5), S1-Ti-S2 $96.1(2)$, S1-Ru-S2 $102.9(2)$, Ti-S1-Ru $80.0(2)$, Ti-S2-Ru $80.4(2)$.



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**),⁶ in 95% yield (eq 3). In the IR spectrum of **2**, an absorption of $\nu(\text{Ru-H})$ was observed at 1937 cm^{-1} . The ^1H 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 ppm .

The complex **1** reacted with AgPF_6 in the presence of ligands L ($\text{L} = t\text{-BuCN}$ or 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**)⁷ in 76 and 11% yields, respectively (eq 4).



To confirm the structure of **3a**, X-ray analysis was performed.⁸ 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**.

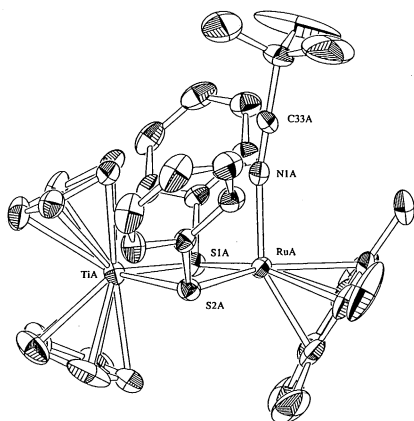


Figure 2. ORTEP drawing of the cation of **3a** [one of the pair of independent molecules (molecule A), 30% probability thermal ellipsoids]. Selected bond lengths [Å] and angles [°]: TiA-S1A 2.459(3), TiA-S2A 2.463(3), RuA-S1A 2.368(2), RuA-S2A 2.370(2), RuA-N1A 2.047(7), S1A-TiA-S2A 95.91(9), S1A-RuA-S2A 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

- 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).
- K. Osakada, Y. Kawaguchi, and T. Yamamoto, *Organometallics*, **14**, 4542 (1995).
- 1**: brown powder. Mp: 143.0-146.0 °C (decomp). ¹H NMR (CDCl₃): 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*). ¹³C NMR (CDCl₃): δ 143.2 (Ph), 131.8 (Ph), 127.8 (Ph), 125.6 (Ph), 110.4 (Cp), 104.3 (Cp), 91.4 (C₅Me₅), 9.9 (C₅Me₅). Anal. Found: C, 57.29; H, 5.51; Cl, 5.74%. Calcd for C₃₂H₃₅ClS₂RuTi: C, 57.52; H, 5.28; Cl, 5.31%.
- X-ray structure analysis of **1**: C₃₂H₃₅ClS₂RuTi, *F.W.*=668.17, space group *P*2₁/*n*, *Z*=4, *a*=12.201(7), *b*=16.718(4), *c*=20.689(4) Å, β=100.34(2)°, *V*=4151(2) Å³, ρ_{calcd}=1.069 gcm⁻³. 9921 measured, 9467 independent reflections, of which 1876 were considered as observed [*I*>3.50σ(*I*)]. *R*=0.072, *R*_w=0.073.
- E. G. Muller, S. F. Watkins, and L. F. Dahl, *J. Organomet. Chem.*, **111**, 73 (1976).
- 2**: brown powder. Mp: 170.0-175.0 °C (decomp). ¹H NMR (CDCl₃): 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). ¹³C NMR (CDCl₃): δ 147.0 (Ph), 125.5 (Ph), 107.5 (Cp), 103.8 (Cp), 94.0 (C₅Me₅), 10.6 (C₅Me₅). IR (KBr): ν(Ru-H), 1937 cm⁻¹.
- 3a**: dark violet crystals. Mp: 143.0-146.3 °C. ¹H NMR (CD₂Cl₂): 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, ^tBu). ¹³C NMR (CD₂Cl₂): δ 141.6 (Ph), 137.4 (CN), 131.0 (Ph), 129.5 (Ph), 127.4 (Ph), 110.8 (Cp), 106.9 (Cp), 93.9 (C₅Me₅), 30.9 (Me₃C), 25.9 (Me₃C), 10.2 (C₅Me₅). Anal. Found: C, 48.15; H, 4.89; N, 1.50%. Calcd for C₃₇H₄₄F₆NPS₂RuTi•CH₂Cl₂: C, 48.16; H, 4.89; N, 1.63%.
- 3b**: dark violet crystals. Mp: 116.0-121.5 °C. ¹H NMR (CD₂Cl₂): 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*). ¹³C NMR (CD₂Cl₂): δ 141.4 (Ph), 130.9 (Ph), 129.5 (Ph), 127.9 (CN), 127.4 (Ph), 110.6 (Cp), 106.6 (Cp), 94.2 (C₅Me₅), 10.1 (C₅Me₅), 4.1 (MeCN). Anal. Found: C, 46.36; H, 4.47; N, 1.57%. Calcd for C₃₄H₃₈F₆NPS₂RuTi•CH₂Cl₂: C, 46.52; H, 4.46; N, 1.55%.
- X-ray structure analysis of **3a**: C₃₇H₄₄F₆NPS₂RuTi•CH₂Cl₂, *F.W.*=945.75, space group *P*1̄, *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) Å³, ρ_{calcd}=1.510 gcm⁻³. 19519 measured, 18865 independent reflections, of which 7920 were considered as observed [*I*>3.00σ(*I*)]. *R*=0.056, *R*_w=0.054.