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Novel Group 4 metal–ruthenium complexes. Synthesis, structure and reactivity of the first thiolato-bridged titanium–ruthenium and zirconium–ruthenium complexes

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Complexes [TiCp$_2$(SR)$_2$] (R = Ph or Me) reacted with [RuCl(Cp*)(cod)] (cod = cycloocta-1,5-diene) to afford [Cp$_2$Ti(μ-SR)$_2$RuCl(Cp*)] (Cp = cyclopentadienyl, Cp* = pentamethylcyclopentadienyl; R = Ph **1a** or Me **1b**). X-Ray analysis of **1a** showed that two phenyl groups on the sulfur atoms are in *syn* conformation. The complex [Cp$_2$Zr(μ-SMe)$_2$RuCl(Cp*)] **1d** was also prepared. Complexes **1a** and **1b** reacted with KBH(Bu^s)$_3$ to afford hydrido complexes [Cp$_2$Ti(μ-SR)$_2$RuH(Cp*)] (R = Ph **2a** or Me **2b**), and with Ag$^+$ in the presence of ligands to afford [Cp$_2$Ti(μ-SR)$_2$Ru(L)Cp*]$^+$X$^-$ (R = Ph, L = CO, X = BF$_4$ **3a**; R = Me, L = CO, X = PF$_6$ **3b**; R = Ph, L = Bu^{t}NC, X = BF$_4$ **4a**; R = Me, L = Bu^{t}NC, X = PF$_6$ **4b**; R = Ph, L = Bu^{t}CN, X = PF$_6$ **5a**; R = Me, L = Bu^{t}CN, X = PF$_6$ **5b**; R = Ph, L = MeCN, X = PF$_6$ **6a**; R = Me, L = MeCN, X = PF$_6$ **6b**). The structures of these cationic complexes were also revealed by X-ray analysis.

Recently, much attention has been paid to heterobimetallic complexes. Particularly the chemistry of early–late heterobimetallics (ELHB)[1] is an interesting area because they contain a d-electron deficient early transition metal and a d-electron rich late transition metal in one molecule, and in view of their potential for co-operative behavior between the metals which could confer unusual reactivity or catalytic properties. The two transition metals would provide an environment for activation of polar substrates.

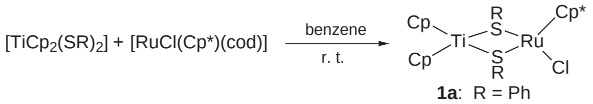
Thiolates have often been used to bridge metallic centers. To prepare thiolato-bridged ELHB complexes,[2] reactions of metalloligand [MCp$_2$(SR)$_2$] (M = early transition metal) with a variety of late transition metal complexes [M′L$_n$] have been investigated. In some cases thiolato-bridged [Cp$_2$M(μ-SR)$_2$-M′L$_n$] was synthesized,[2d–o] and in other cases thiolate ligand transfer occurred giving [M′(SR)$_2$L$_n$].[2k,3]

On the other hand, the chemistry of organoruthenium complexes is a productive area.[4] Such complexes have been prepared, and their reactivities and catalytic activities revealed, but no thiolato-bridged Ru–Group 4 metal complex is known. In this paper we report the synthesis, structure and reactivity of the first thiolato-bridged Group 4 metal (Ti or Zr)–ruthenium complexes. Preliminary results have been reported briefly in a communication.[2p]

Results and Discussion

Preparation of [Cp$_2$Ti(μ-SR)$_2$RuCl(Cp*)]

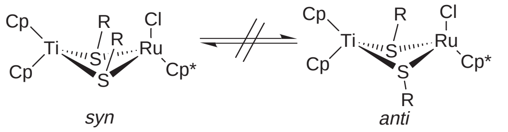
The reaction of [TiCp$_2$(SR)$_2$] with [RuCl(Cp*)(cod)] in benzene liberated cod to give novel thiolato-bridged complexes [Cp$_2$-Ti(μ-SR)$_2$RuCl(Cp*)] (R = Ph **1a** or Me **1b**) in 79 and 81% yield, respectively, equation (1). The ^{1}H and ^{13}C NMR data of



(1)

1a: R = Ph
1b: R = Me

these complexes are summarized in Table 1. The spectra showed resonances for two non-equivalent Cp rings on Ti (δ 5.44 and 5.16 for **1a**, 5.62 and 5.03 for **1b**) at higher field than that of the starting complexes [TiCp$_2$(SR)$_2$] (δ 6.03 for R = Ph, 6.13 for R = Me), which indicates electron donation from the Cp*-Ru(SR)$_2$ group to Cp$_2$Ti. Resonances for two SR groups were found equivalently at δ 7.90–7.11 (Ph, **1a**) and 2.50 (Me, **1b**). The resonances for Cp* were at δ 1.65 (**1a**) and 1.61 (**1b**), at lower field than that of [RuCl(Cp*)(cod)] (δ 1.58). Considering these NMR data, the complexes **1a** and **1b** were deduced to be thiolato-bridged heterobimetallic complexes [Cp$_2$Ti(μ-SR)$_2$-RuCl(Cp*)]. No temperature dependence of the NMR spectra in the range 353–298 K was observed. The NMR study and the X-ray analysis of **1a** (see below) indicate that two substituents (Ph or Me) on sulfur are in *syn* conformation even in solution. The *syn*–*anti* interconversion [equation (2)] discussed for [Cp$_2$Ti(μ-SEt)$_2$CuL][PF$_6$] (L = PPh$_3$, PCy$_3$, PEt$_3$, *etc.*)[2i] and [Cp$_2$Ti-(μ-SMe)$_2$Cu(MeCN)$_2$][PF$_6$][2l] was not observed.



(2)

Crystal structure of complex 1a

To confirm the structure of these complexes, an X-ray analysis of **1a** was performed. The molecular geometry and atom-numbering system are shown in Fig. 1, while Tables 2 and 3 summarize the results obtained. The geometries around the Ti and Ru are pseudo-tetrahedral and three-legged pianostool, respectively. The complex **1a** has a four-membered ring of Ti, Ru and two S atoms. The TiS$_2$Ru core is slightly puckered, with an angle of 9.11° between the S(1)–Ti–S(2) and the S(1)–Ru–S(2) planes. Two phenyl groups on the sulfur atoms are in *syn* conformation. The Ti–S distances of 2.464(6) and 2.468(5) are somewhat longer than those observed for [TiCp$_2$(SPh)$_2$] [2.395(8), 2.424(8) Å].[6] The S–Ti–S angle [96.1(2)°] is slightly smaller than that for [TiCp$_2$(SPh)$_2$] [99.3(3)°].[6] The Ti–S–Ru angles in **1a** are 80.4(2) and 80.0(2)°. Angles at bridging atoms of less than 80° have been cited as evidence for metal–metal interaction.[1b,2a,g,7] The angles at the sulfur atoms of **1a** are on the border. The Ti···Ru distance is 3.101(4) Å, larger than the sum of the atomic radii (2.70 Å),[8] but shorter than the corresponding distance found in the isoelectronic Ti^{IV}–Mo^0 complex, [Cp$_2$Ti(μ-SMe)$_2$Mo(CO)$_4$] [3.321(2) Å].[9]

Table 1 Proton and ^{13}C NMR data for complexes **1**–**6**

Complex	^{1}H NMR (δ)	^{13}C NMR (δ)
1a^a	7.90–7.11 (m, 10 H, Ph), 5.44 (s, 5 H, C_5H_5), 5.16 (s, 5 H, C_5H_5), 1.65 (s, 15 H, C_5Me_5)	143.2, 131.8, 127.8, 125.6 (Ph), 110.4, 104.3 (C_5H_5), 91.4 ($\mathit{C}_5\mathrm{Me}_5$), 9.9 ($\mathrm{C}_5\mathit{Me}_5$)
1b^a	5.62 (s, 5 H, C_5H_5), 5.03 (s, 5 H, C_5H_5), 2.50 (s, 6 H, SMe), 1.61 (s, 15 H, C_5Me_5)	106.3, 104.2 (C_5H_5), 89.8 ($\mathit{C}_5\mathrm{Me}_5$), 19.5 (SMe), 9.5 ($\mathrm{C}_5\mathit{Me}_5$)
1c^a	7.93–7.17 (m, 10 H, Ph), 5.52 (s, 5 H, Ti–C_5H_5), 5.24 (s, 5 H, Ti–C_5H_5), 4.95 (s, 5 H, Ru–C_5H_5)	143.0, 131.9, 128.1, 126.1 (Ph), 110.4, 105.3 (Ti–C_5H_5), 80.8 (Ru–C_5H_5)
1d^c	5.82 (s, 5 H, C_5H_5), 5.31 (s, 5 H, C_5H_5), 2.31 (s, 6 H, SMe), 1.55 (s, 15 H, C_5Me_5)	107.7, 105.1 (C_5H_5), 89.0 ($\mathit{C}_5\mathrm{Me}_5$), 16.4 (SMe), 9.4 ($\mathrm{C}_5\mathit{Me}_5$)
2a^a	7.75–7.09 (m, 10 H, Ph), 5.25 (s, 5 H, C_5H_5), 4.59 (s, 5 H, C_5H_5), 1.78 (s, 15 H, C_5Me_5), −14.46 (s, 1 H, Ru–H)	147.0, 125.5 (Ph), 107.5, 103.8 (C_5H_5), 94.0 ($\mathit{C}_5\mathrm{Me}_5$), 10.6 ($\mathrm{C}_5\mathit{Me}_5$)
2b^b	5.34 (s, 5 H, C_5H_5), 4.91 (s, 5 H, C_5H_5), 2.24 (s, 6 H, SMe), 1.83 (s, 15 H, C_5Me_5), −16.71 (s, 1 H, Ru–H)	105.1, 104.8 (C_5H_5), 93.8 ($\mathit{C}_5\mathrm{Me}_5$), 31.9 (SMe), 11.1 ($\mathrm{C}_5\mathit{Me}_5$)
3a^c	7.51–7.34 (m, 10 H, Ph), 5.87 (s, 5 H, C_5H_5), 5.21 (s, 5 H, C_5H_5), 1.93 (s, 15 H, C_5Me_5)	202.5 (Ru–CO), 139.8, 130.6, 130.0, 128.3 (Ph), 113.3, 109.0 (C_5H_5), 102.8 ($\mathit{C}_5\mathrm{Me}_5$), 10.6 ($\mathrm{C}_5\mathit{Me}_5$)
3b^c	5.79 (s, 5 H, C_5H_5), 5.41 (s, 5 H, C_5H_5), 2.69 (s, 6 H, SMe), 1.90 (s, 15 H, C_5Me_5)	202.0 (Ru–CO), 109.4, 108.2 (C_5H_5), 101.9 ($\mathit{C}_5\mathrm{Me}_5$), 27.4 (SMe), 10.3 ($\mathrm{C}_5\mathit{Me}_5$)
4a^c	7.51–7.28 (m, 10 H, Ph), 5.68 (s, 5 H, C_5H_5), 5.09 (s, 5 H, C_5H_5), 1.84 (s, 15 H, C_5Me_5), 1.23 (s, 9 H, Me_3CNC)	149.3 ($\mathrm{Me_3CN}\mathit{C}$), 141.5, 131.0, 129.4, 127.6 (Ph), 111.5, 107.1 (C_5H_5), 98.8 ($\mathit{C}_5\mathrm{Me}_5$), 58.6 ($\mathrm{Me_3}\mathit{C}\mathrm{NC}$), 30.5 ($\mathit{Me}_3\mathrm{CNC}$), 10.5 ($\mathrm{C}_5\mathit{Me}_5$)
4b^c	5.62 (s, 5 H, C_5H_5), 5.23 (s, 5 H, C_5H_5), 2.51 (s, 6 H, SMe), 1.80 (s, 15 H, C_5Me_5), 1.36 (s, 9 H, Me_3CNC)	153.6 ($\mathrm{Me_3CN}\mathit{C}$), 107.5, 106.7 ($C_5H_5$), 97.9 ($\mathit{C}_5\mathrm{Me}_5$), 58.3 ($\mathrm{Me_3}\mathit{C}\mathrm{NC}$), 30.7 ($\mathit{Me}_3\mathrm{CNC}$), 25.2 (SMe), 10.1 ($\mathrm{C}_5\mathit{Me}_5$)
5a^c	7.44–7.26 (m, 10 H, Ph), 5.63 (s, 5 H, C_5H_5), 5.07 (s, 5 H, C_5H_5), 1.73 (s, 15 H, C_5Me_5), 1.07 (s, 9 H, Me_3CCN)	141.6 (Ph), 137.4 ($\mathrm{Me_3C}\mathit{C}\mathrm{N}$), 131.0, 129.5, 127.4 (Ph), 110.8, 106.9 (C_5H_5), 93.9 ($\mathit{C}_5\mathrm{Me}_5$), 30.9 ($\mathrm{Me_3}\mathit{C}\mathrm{CN}$), 25.9 ($\mathit{Me}_3\mathrm{CCN}$), 10.2 ($\mathrm{C}_5\mathit{Me}_5$)
5b^{c,d}	5.46 (s, 5 H, C_5H_5), 5.09 (s, 5 H, C_5H_5), 2.24 (s, 6 H, SMe), 1.60 (s, 15 H, C_5Me_5), 1.21 (s, 9 H, Me_3CCN)	133.6 ($\mathrm{Me_3C}\mathit{C}\mathrm{N}$), 105.9 ($C_5H_5$), 105.6 ($C_5H_5$), 91.8 ($\mathit{C}_5\mathrm{Me}_5$), 30.2 ($\mathrm{Me_3}\mathit{C}\mathrm{CN}$), 20.8 (SMe), 20.8 ($\mathit{Me}_3\mathrm{CCN}$), 9.1 ($\mathrm{C}_5\mathit{Me}_5$)
6a^c	7.41–7.26 (m, 10 H, Ph), 5.59 (s, 5 H, C_5H_5), 4.99 (s, 5 H, C_5H_5), 2.03 (s, 3 H, MeCN), 1.74 (s, 15 H, C_5Me_5)	141.4, 130.9, 129.5 (Ph), 127.9 ($\mathrm{Me}\mathit{C}\mathrm{N}$), 127.4 (Ph), 110.6, 106.6 (C_5H_5), 94.2 ($\mathit{C}_5\mathrm{Me}_5$), 10.1 ($\mathrm{C}_5\mathit{Me}_5$), 4.1 ($\mathit{Me}\mathrm{CN}$)
6b^{c,d}	5.42 (s, 5 H, C_5H_5), 5.06 (s, 5 H, C_5H_5), 2.41 (s, 3 H, MeCN), 2.25 (s, 6 H, SMe), 1.57 (s, 15 H, C_5Me_5)	127.9 ($\mathrm{Me}\mathit{C}\mathrm{N}$), 106.4 ($C_5H_5$), 105.8 ($C_5H_5$), 92.0 ($\mathit{C}_5\mathrm{Me}_5$), 21.4 (SMe), 9.2 ($\mathrm{C}_5\mathit{Me}_5$), 4.1 ($\mathit{Me}\mathrm{CN}$)

^{a} In $CDCl_3$. ^{b} In [$^2H_8$]thf. ^{c} In CD_2Cl_2. ^{d} At 243 K.

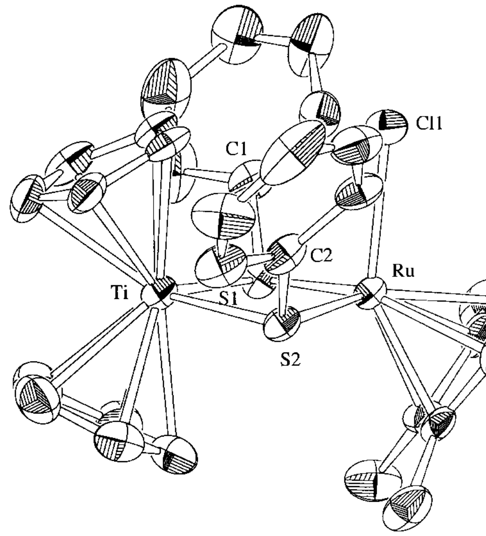
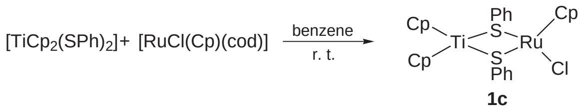


Fig. 1 An ORTEP[5] drawing of [$Cp_2Ti(\mu\text{-}SPh)_2RuCl(Cp^*)$] **1a**

Preparation of [$Cp_2Ti(\mu\text{-}SPh)_2RuCl(Cp)$]

The analogous Cp complex [$Cp_2Ti(\mu\text{-}SPh)_2RuCl(Cp)$] **1c** was prepared in a similar manner to that for **1a** and **1b**. Reaction of [$TiCp_2(SPh)_2$] with [RuCl(Cp)(cod)] afforded **1c** in 24% yield, equation (3). The ^{1}H and ^{13}C NMR data of **1c** are summarized



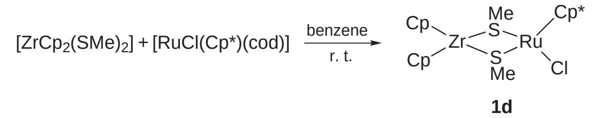
(3)

1c

in Table 1. The ^{1}H NMR spectrum showed resonances for two non-equivalent Cp rings on Ti at δ 5.52 and 5.24. Resonances for two SPh were found equivalently at δ 7.93–7.17. The resonances for the Cp ring on Ru were at δ 4.95. Similarly to **1a** and **1b**, no temperature dependence of the NMR spectrum in the range 353–298 K was observed.

Preparation of [$Cp_2Zr(\mu\text{-}SMe)_2RuCl(Cp^*)$]

The analogous Zr–Ru complex [$Cp_2Zr(\mu\text{-}SMe)_2RuCl(Cp^*)$] **1d** was prepared in a similar manner to that for **1a**, **1b** and **1c**. The known complex [$ZrCp_2(SMe)_2$][10] was prepared by reaction of [$ZrCl_2Cp_2$] with 2 equivalents of NaSMe in thf. The reaction of [$ZrCp_2(SMe)_2$] with [RuCl(Cp*)(cod)] in benzene liberated cod to give [$Cp_2Zr(\mu\text{-}SMe)_2RuCl(Cp^*)$] **1d** in 60% yield, equation (4). Reaction of [$ZrCp_2(SPh)_2$] with [RuCl(Cp*)(cod)] was also attempted but no isolable product was obtained.



(4)

1d

The ^{1}H NMR spectra of complex **1d** showed resonances for two non-equivalent Cp rings on Zr at δ 5.82 and 5.31, at higher field than those of the starting complex [$ZrCp_2(SMe)_2$] (δ 6.21). This observation indicates electron donation from the Cp*Ru-$(SMe)_2$ group to Cp_2Zr. Resonances for the two SMe groups were found equivalently at δ 2.31 and for Cp* at δ 1.55. Considering these NMR data, the complex **1d** was deduced to be the thiolato-bridged Zr–Ru complex [$Cp_2Zr(\mu\text{-}SMe)_2RuCl(Cp^*)$].

Crystal structure of complex 1d

To confirm the structure of complex **1d** an X-ray analysis was performed. The molecular geometry and atom-numbering system are shown in Fig. 2, while Tables 2 and 3 summarize the results obtained. In the unit cell there are two independent molecules A and B, which are very similar to each other. The geometries around the Zr and Ru are pseudo-tetrahedral and

Table 2 Selected bond lengths (Å) and angles (°) in complexes **1a**, **1d**, **4a**, **5a**·CH_2Cl_2 and **5b**

	1a[a]	**1d**[b,c]	**4a**[a]	**5a**·CH_2Cl_2[a,c]	**5b**[a]
M···Ru	3.101(4)	3.097(2), 3.089(2)	3.160(2)	3.141(2), 3.097(3)	3.134(2)
M–S(1)	2.464(6)	2.512(5), 2.546(6)	2.458(2)	2.459(3), 2.472(3)	2.447(2)
M–S(2)	2.468(5)	2.548(6), 2.524(5)	2.457(2)	2.463(3), 2.467(3)	2.457(2)
Ru–S(1)	2.338(5)	2.373(5), 2.361(5)	2.362(2)	2.368(2), 2.362(2)	2.366(2)
Ru–S(2)	2.353(5)	2.363(5), 2.365(5)	2.359(2)	2.370(2), 2.362(2)	2.365(2)
Ru–Cl(1)	2.451(5)	2.462(5), 2.454(6)			
Ru–C(3)			1.936(7)		
Ru–N(1)				2.047(7), 2.055(7)	2.040(7)
S(1)–C(1)	1.77(3)	1.80(2), 1.84(2)	1.792(7)	1.784(8), 1.792(8)	1.815(10)
S(2)–C(2)	1.76(2)	1.85(2), 1.77(2)	1.800(8)	1.776(8), 1.791(9)	1.80(1)
C(3)–N(1)			1.154(9)	1.131(9), 1.131(9)	1.14(1)
S(1)–M–S(2)	96.1(2)	97.0(2), 96.9(2)	94.64(7)	95.91(9), 97.07(9)	96.43(8)
S(1)–Ru–S(2)	102.9(2)	106.3(2), 106.9(2)	99.86(7)	100.96(8), 103.18(8)	101.24(7)
M–S(1)–Ru	80.4(2)	78.6(2), 77.9(2)	81.89(7)	81.17(8), 79.65(7)	81.25(7)
M–S(1)–C(1)	119.1(8)	120.6(7), 115.5(7)	119.0(3)	119.3(3), 118.2(3)	119.4(3)
Ru–S(1)–C(1)	122.9(9)	111.8(8), 110.4(6)	118.0(3)	117.4(3), 119.0(3)	108.5(3)
M–S(2)–Ru	80.0(2)	78.1(2), 78.3(2)	81.98(7)	81.05(8), 79.75(8)	81.06(7)
M–S(2)–C(2)	117.1(7)	115.8(7), 119.6(7)	120.6(3)	118.9(3), 118.2(3)	120.0(4)
Ru–S(2)–C(2)	122.9(9)	112.1(8), 113.1(8)	116.9(3)	120.0(3), 117.5(3)	109.1(4)
S(1)–Ru–Cl(1)	95.6(2)	91.9(2), 92.8(2)			
S(2)–Ru–Cl(1)	96.0(2)	92.6(2), 91.8(2)			
S(1)–Ru–C(3)			96.3(2)		
S(2)–Ru–C(3)			94.9(2)		
S(1)–Ru–N(1)				94.6(2), 94.3(2)	91.0(2)
S(2)–Ru–N(1)				93.9(2), 93.0(2)	92.5(2)
Ru–C(3)–N(1)			172.6(6)		
Ru–N(1)–C(3)				169.5(7), 170.7(7)	169.4(7)

[a] M = Ti. [b] M = Zr. [c] There are two independent molecules (A and B) in the unit cell.

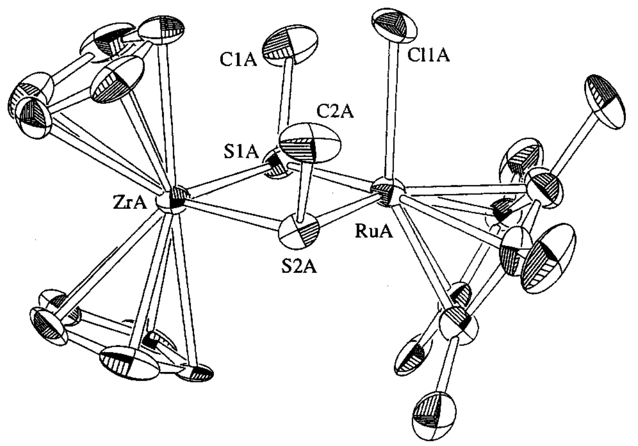
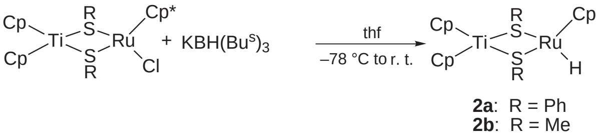


Fig. 2 An ORTEP drawing of $[Cp_2Zr(\mu\text{-}SMe)_2RuCl(Cp^*)]$ **1d** (one of the pair of independent molecules, A)

three-legged pianostool, respectively. The complex **1d** has a four-membered ring of Zr, Ru and two S atoms. The four atoms of the ZrS_2Ru core lie on a plane, with the mean deviation from the least-squares plane being 0.0097 (molecule A) and 0.0032 Å (B), respectively. This is very different from **1a**. Two methyl groups on the sulfur atoms of each molecule are in *syn* conformation, similar to Ti–Ru complexes. The Zr–S(1), Zr–S(2), Ru–S(1) and Ru–S(2) lengths for A and B are 2.512(5) and 2.546(6), 2.548(6) and 2.524(5), 2.373(5) and 2.361(5), 2.363(5) and 2.365(5) Å, respectively. The Zr–S–Ru angles are 78.6(2) and 78.1(2) (molecule A), 77.9(2) and 78.3(2)° (B). The Zr···Ru distances are 3.097(2) and 3.089(2) Å, larger than the sum of the atomic radii (2.85 Å),[8] but shorter than the Ti···Ru distances in thiolato bridged complexes (3.10–3.16 Å), though the atomic radii are 1.40 (Ti) and 1.55 Å (Zr).[8] Considering the angles at the bridging sulfur atoms and Zr···Ru distances, a dative interaction between Zr and Ru is strongly suggested.

Reaction of complex 1a or 1b with $KBH(Bu^s)_3$

Complex **1a** or **1b** reacted with $KBH(Bu^s)_3$ to give hydrido complexes, $[Cp_2Ti(\mu\text{-}SPh)_2RuH(Cp^*)]$ (R = Ph **2a** or Me **2b**), in 95 and 34% yields, respectively, equation (5). In the IR spectra



(5)

of **2a** and **2b** ν(Ru–H) is observed at 1937 and 1900 cm^{-1}, respectively. The ^1H NMR spectra showed non-equivalent Cp resonances at δ 5.25 and 4.59 for **2a**, 5.34 and 4.91 for **2b**, at higher field than those for **1a** and **1b**. The signals of Cp* were observed at lower field than those of the parent complexes. The signals assigned to the hydrides on Ru were observed at δ −14.46 (**2a**) and −16.71 (**2b**), respectively. Reaction of **1d** with $KBH(Bu^s)_3$ was also attempted, and the formation of an analogous hydrido complex was confirmed by NMR spectra, but the product could not be isolated probably because of its instability.

Reaction of complex 1a or 1b with Ag^+ in the presence of ligands

Complex **1a** or **1b** reacted with $AgBF_4$ or $AgPF_6$ in the presence of ligands such as CO, Bu^tNC or nitriles to afford hetero-bimetallic cationic complexes $[Cp_2Ti(\mu\text{-}SR)_2Ru(L)Cp^*]^+X^-$ (R = Ph, L = CO, X = BF_4 **3a**; R = Me, L = CO, X = PF_6 **3b**; R = Ph, L = Bu^tNC, X = BF_4 **4a**; R = Me, L = Bu^tNC, X = PF_6 **4b**; R = Ph, L = Bu^tCN, X =PF_6 **5a**; R = Me, L = Bu^tCN, X = PF_6 **5b**; R = Ph, L = MeCN, X = PF_6 **6a**; R = Me; L = MeCN, X = PF_6 **6b**), equation (6).

The ^1H and ^{13}C NMR data of these cationic complexes are summarized in Table 1. The IR spectra of **3a** and **3b** showed absorptions of the co-ordinated carbonyls at 1951 and 1947 cm^{-1}, respectively. The ^1H NMR signal patterns of **3a** and **3b** for Cp, SR and Cp* were similar to those of **1a** and **1b**, but each chemical shift was at lower field than those of **1a** and **1b**. The

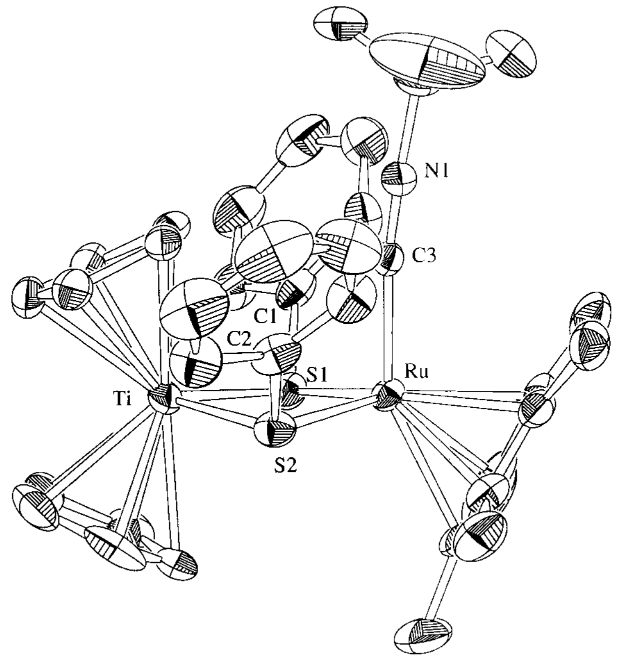
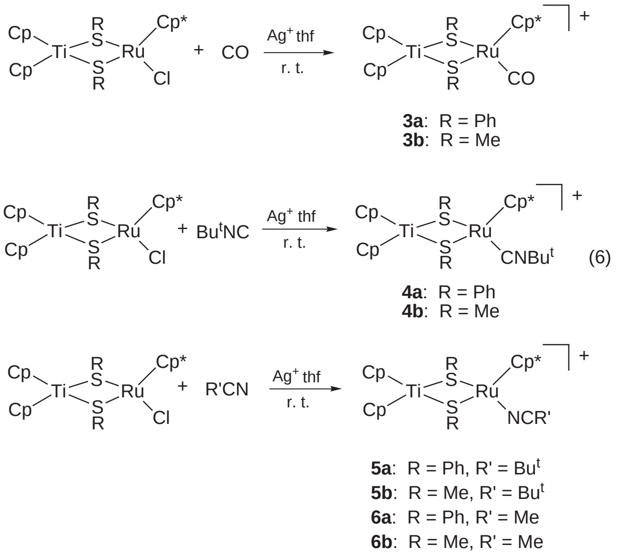


Fig. 3 An ORTEP drawing of the cation $[Cp_2Ti(\mu\text{-}SPh)_2Ru(Bu^tNC)Cp^*]^+$ in the complex **4a**



IR spectra of **4a** and **4b** showed absorptions of isocyanide at 2122 and 2116 cm^{-1}, respectively. A variable-temperature ^1H NMR study for these cationic complexes was performed in the range 348–243 K. For the complexes with carbonyl or isocyanide ligand, **3a**, **3b**, **4a** and **4b**, no temperature dependence was observed. For those with nitrile ligand, **5a** and **6a**, at higher temperature (348 K) two very broad Cp signals and a slightly broad signal for Bu^t (**5a**) or Me (**6a**) were observed, while they were sharp signals at 298 K, and no temperature dependence of the signals for SPh and Cp* was observed. We consider this fluxionality is caused by the weakened bonding between Ru and nitrile ligand, but the details are not clear. A similar temperature dependence was observed for **5b** and **6b**, but their spectra showed broad signals for Cp and nitrile ligands even at 298 K. Those signals sharpened at 243 K. At higher temperature (348 K) decomposition of the complexes occurred. Reactions of the Zr–Ru complex **1d** with $AgPF_6$ in the presence of ligands were also attempted, but the products could not be isolated probably because of their instability.

Crystal structures of complexes 4a, 5a and 5b

To confirm the structures of these cationic complexes, X-ray analyses of **4a**, **5a** and **5b** were performed. The molecular geometry and atom-numbering system are shown in Figs. 3–5, while Tables 2 and 3 summarize the results obtained. For **5a**, 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. These complexes have a four membered TiS_2Ru ring. For **4a** and **5a** this ring is puckered with a dihedral angle of 14.59 (**4a**), 10.97 and 6.97° (**5a**) between the S(1)–Ti–S(2) and the S(1)–Ru–S(2) planes. For **5b** the TiS_2Ru ring is almost planar. This difference is probably because of the substituents on sulfur. In the cases where the substituents are phenyl groups steric demands cause the puckering of the TiS_2Ru ring. For each complex the substituents on sulfur are in *syn* conformation similar to that in complex **1a**. Distances and angles of the TiS_2Ru core are similar to those of **1a**.

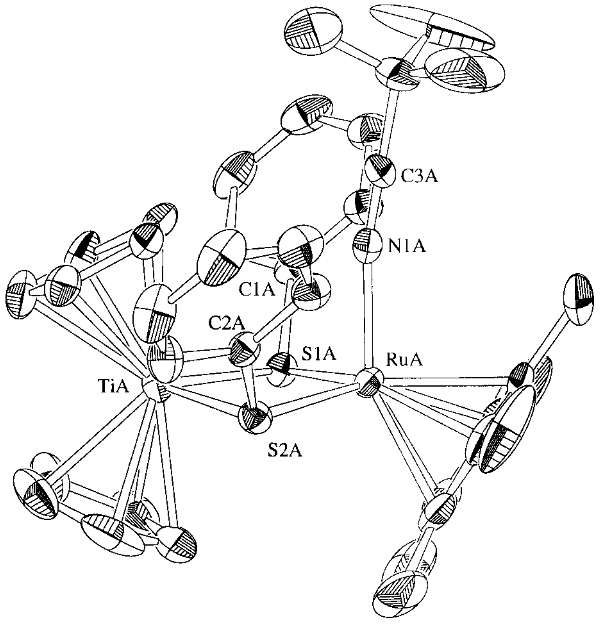


Fig. 4 An ORTEP drawing of the cation $[Cp_2Ti(\mu\text{-}SPh)_2Ru(Bu^tCN)Cp^*]^+$ in the complex $\mathbf{5a}\cdot CH_2Cl_2$ (one of the pair of independent molecules, A)

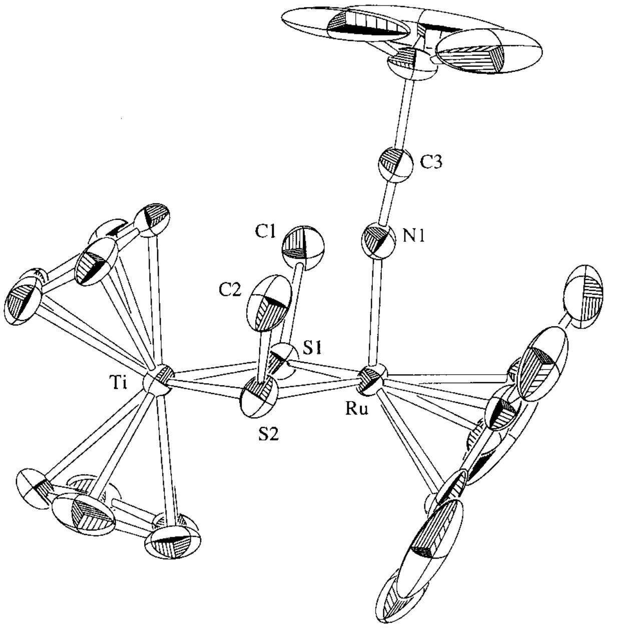


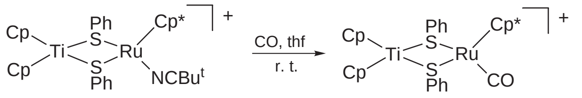
Fig. 5 An ORTEP drawing of the cation $[Cp_2Ti(\mu\text{-}SMe)_2Ru(Bu^tCN)Cp^*]^+$ in the complex **5b**

Reactions of complex 1a or 5a with CO

Complex **1a** reacted with CO (1 atm, 101 325 Pa) at room temperature to give $[TiCp_2(SPh)_2]$ and $[RuCl(Cp^*)(CO)_2]$, equation (7). Cleavage of the Ru–S bond and co-ordination of two carbon monoxides to the co-ordinatively unsaturated ruthenium center occurred, and the TiS_2Ru core was broken. On the other hand, the reaction of cationic complex **5a** with CO (1 atm) gave $[Cp_2Ti(\mu\text{-}SPh)_2Ru(CO)Cp^*]^+$, equation (8). Only ligand substitution on Ru occurred, and the TiS_2Ru core was not broken. This difference of the reactivity of **1a** and **5a** towards CO indicates that the Ru–S bonds in the cationic complex **5a** are much stronger than those in the neutral complex **1a**, although no difference in the distances of Ti–S or Ru–S was observed in the molecular structures.

(7)

1a



(8)

5a

In conclusion, the first thiolato-bridged Group 4 metal–ruthenium complexes were prepared and their structures and reactivities revealed. The complementary reactivities of the early and late transition metals in **1**–**6** are expected. Further investigation on reactivities of these complexes is in progress.

Experimental

All manipulations were performed under a dry argon atmosphere with standard Schlenk techniques. Dichloromethane was distilled from $CaCl_2$, thf from benzophenone ketyl, pentane, hexane and benzene from sodium. The complexes $[TiCp_2(SPh)_2]$,[11] $[TiCp_2(SMe)_2]$,[2k,12] $[RuCl(Cp^*)(cod)]$[13] and $[RuCl(Cp)(cod)]$[14] were prepared by the literature methods. Other reagents were used as obtained from commercial sources. Melting points were determined under air on a Yanagimoto micro melting point apparatus. Elemental analyses were carried out at the Microanalysis Center of Kyoto University. Infrared spectra were recorded on a Shimadzu FTIR-8100 spectrometer and calibrated with a polystyrene standard, ^1H and ^{13}C NMR spectra on a JEOL GSX-270 or a JEOL EX-400 spectrometer.

Preparations

$[Cp_2Ti(\mu\text{-}SR)_2RuCl(Cp^*)]$ (R = Ph 1a or Me 1b). To a mixture of $[TiCp_2(SPh)_2]$ (1.48 g, 3.73 mmol) and $[RuCl(Cp^*)(cod)]$ (1.42 g, 3.73 mmol) was added benzene (50 cm^3) at room temperature. Stirring the mixture at room temperature for 24 h caused a change from purple to brown. After evaporation of the solvent, washing the residue with hexane (100 cm^3) gave $[Cp_2Ti(\mu\text{-}SPh)_2RuCl(Cp^*)]$ **1a** (1.96 g, 79%) as a brown powder, m.p. 143.0–146.0 °C (decomp.) (Found: C, 57.29; H, 5.51; Cl, 5.74. $C_{32}H_{35}ClRuS_2Ti$ requires C, 57.52; H, 5.28; Cl, 5.31%). Similar reaction of $[TiCp_2(SMe)_2]$ with $[RuCl(Cp^*)(cod)]$ gave $[Cp_2Ti(\mu\text{-}SMe)_2RuCl(Cp^*)]$ **1b** (81%), m.p. 171.2–173.7 °C (decomp.) (Found: C, 48.56; H, 5.72; Cl, 6.52. $C_{22}H_{31}ClRuS_2Ti$ requires C, 48.57; H, 5.74; Cl, 6.52%).

$[Cp_2Ti(\mu\text{-}SPh)_2RuCl(Cp)]$ 1c. To a mixture of $[TiCp_2(SPh)_2]$ (0.056 g, 0.14 mmol) and $[RuCl(Cp)(cod)]$ (0.043 g, 0.14 mmol) was added benzene (3 cm^3) at room temperature. Stirring the mixture at room temperature for 15 h caused a change from purple to brown. After evaporation of the solvent, washing the residue with pentane (6 cm^3) gave $[Cp_2Ti(\mu\text{-}SPh)_2RuCl(Cp)]$ **1c** (0.020 g, 24%) as a brown powder, m.p. 142.3–146.1 °C.

$[ZrCp_2(SMe)_2]$. Although the preparation of $[ZrCp_2(SMe)_2]$ has been reported,[10] we used another method. To $[ZrCl_2Cp_2]$ (0.72 g, 2.5 mmol) in thf (30 cm^3) was added NaSMe (0.39 g, 5.5 mmol) and the mixture stirred for 12 h. After filtration, evaporation of the solvent and washing with pentane (30 cm^3) gave $[ZrCp_2(SMe)_2]$ (0.53 g, 68%); $\delta_H(CDCl_3)$ 6.21 (10 H, s, C_5H_5) and 2.52 (6 H, s, SMe).

$[Cp_2Zr(\mu\text{-}SMe)_2RuCl(Cp^*)]$ 1d. To a mixture of $[ZrCp_2(SMe)_2]$ (0.16 g, 0.51 mmol) and $[RuCl(Cp^*)(cod)]$ (0.20 g, 0.52 mmol) was added benzene (7 cm^3) at room temperature. Stirring the mixture at room temperature for 13 h caused a change from orange-yellow to dark brown. After evaporation of the solvent, washing the residue with pentane (28 cm^3) gave $[Cp_2Zr(\mu\text{-}SMe)_2RuCl(Cp^*)]$ **1d** (0.18 g, 60%) as a yellow powder, m.p. 150.4–154.0 °C (decomp.) (Found: C, 44.71; H, 5.20. $C_{22}H_{31}ClRuS_2Zr$ requires C, 44.99; H, 5.32%).

$[Cp_2Ti(\mu\text{-}SR)_2RuH(Cp^*)]$ (R = Ph 2a or Me 2b). To a solution of complex **1a** (0.98 g, 1.5 mmol) in thf (30 cm^3) was added a thf solution of $KBH(Bu^s)_3$ (1.0 M, 1.5 cm^3, 1.5 mmol) at −78 °C, and then stirred at room temperature for 1 h. After evaporation of the solvent, the residue was extracted with benzene (15 cm^3). Evaporation of the solvent gave a brown powder of $[Cp_2Ti(\mu\text{-}SPh)_2RuH(Cp^*)]$ **2a** (0.88 g, 95%), m.p. 170.0–175.0 °C (decomp.) (Found: C, 60.36; H, 5.72. $C_{32}H_{36}RuS_2Ti$ requires C, 60.65; H, 5.73%); $\tilde{\nu}/cm^{-1}$ (Ru–H) 1937m (KBr). Similar reaction of **1b** gave a brown powder of $[Cp_2Ti(\mu\text{-}SMe)_2RuH(Cp^*)]$ **2b** (34%), m.p. 239.5–243.1 °C (decomp.); $\tilde{\nu}/cm^{-1}$ (Ru–H) 1900m (KBr). Elemental analyses for **2b** were unsatisfactory because of a small amount of contaminant. Similar reaction of **1d** was also attempted, and the formation of an analogous hydrido complex was confirmed by the ^1H NMR spectrum in solution, but the product could not be isolated; $\delta_H(CDCl_3)$ 5.57 (5 H, s, C_5H_5), 5.14 (5 H, s, C_5H_5), 2.14 (6 H, s, SMe), 1.74 (15 H, s, C_5Me_5) and −15.86 (1 H, s, Ru–H).

$[Cp_2Ti(\mu\text{-}SR)_2Ru(CO)Cp^*][X]$ (R = Ph, X = BF_4 3a; R = Me, X = PF_6 3b). A mixture of complex **1a** (0.28 g, 0.42 mmol) and $AgBF_4$ (0.083 g, 0.42 mmol) was placed in a flask (50 cm^3). After evacuation, the system was filled with CO (1 atm). Then thf (15 cm^3) was added and the solution stirred at room temperature for 4 h. A change from brown to red was accompanied by precipitation of a dark red powder. The precipitate was filtered off and washed with thf (4 cm^3). Then the precipitate was collected and extracted with dichloromethane (15 cm^3). Evaporation of the solvent gave a dark red powder of $[Cp_2Ti(\mu\text{-}SPh)_2Ru(CO)Cp^*][BF_4]$ **3a** (0.15 g, 49%), m.p. 211.4–212.0 °C (decomp.) (Found: C, 49.29; H, 4.67. $C_{33}H_{35}BF_4ORuS_2Ti\cdot CH_2Cl_2$ requires C, 49.00; H, 4.48%); $\tilde{\nu}/cm^{-1}$ (CO) 1951s (KBr). Similar reaction of **1b** with $AgPF_6$ in the presence of CO gave a dark red powder of $[Cp_2Ti(\mu\text{-}SMe)_2Ru(CO)Cp^*][PF_6]$ **3b** (63%), m.p. 201.7–207.3 °C (decomp.) (Found: C, 40.27; H, 4.51. $C_{23}H_{31}F_6OPRuS_2Ti$ requires C, 40.53; H, 4.58%); $\tilde{\nu}/cm^{-1}$ (CO) 1947s (KBr).

$[Cp_2Ti(\mu\text{-}SR)_2Ru(Bu^tNC)Cp^*][X]$ (R = Ph, X = BF_4 4a; R = Me, X = PF_6 4b). To a mixture of complex **1a** (0.32 g, 0.48 mmol) and $AgBF_4$ (0.095 g, 0.49 mmol) was added thf (15 cm^3). Then Bu^tNC (0.060 cm^3, 0.53 mmol) was added immediately, and the solution stirred at room temperature for 4 h. It changed from brown to red accompanied by precipitation of a dark red powder. The precipitate was filtered off, washed with thf (4 cm^3) and extracted with dichloromethane (15 cm^3). Evaporation of the solvent gave a dark red powder of $[Cp_2Ti(\mu\text{-}SPh)_2Ru(Bu^tNC)Cp^*][BF_4]$ **4a** (0.24 g, 61%), m.p. 273.3–274.0 °C

Table 3 Summary of crystal data, collection data and refinement of complexes **1a**, **1d**, **4a**, **5a**·CH_2Cl_2 and **5b**

	1a	**1d**	**4a**	**5a**·CH_2Cl_2	**5b**
Color	Brown	Yellow	Dark red	Dark violet	Dark violet
Habit	Prismatic	Plate	Plate	Needle	Needle
Maximum dimensions/mm	0.40 × 0.20 × 0.10	0.20 × 0.15 × 0.05	0.40 × 0.40 × 0.10	0.40 × 0.10 × 0.05	0.50 × 0.20 × 0.20
Formula	$C_{32}H_{35}ClRuS_2Ti$	$C_{22}H_{31}ClRuS_2Zr$	$C_{37}H_{44}BF_4NRuS_2Ti$	$C_{37}H_{46}Cl_2F_6NPRuS_2Ti$	$C_{27}H_{40}F_6NPRuS_2Ti$
M	668.17	587.35	802.65	933.74	736.67
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/n$	$C2/c$	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$
T/°C	20 ± 1	23 ± 1	23 ± 1	23 ± 1	23 ± 1
a/Å	12.201(7)	46.538(6)	12.658(3)	16.567(4)	16.545(4)
b/Å	16.718(4)	8.458(6)	19.531(5)	22.618(7)	22.961(8)
c/Å	20.689(4)	31.631(5)	14.820(5)	11.885(8)	8.326(4)
α/°				102.90(5)	
β/°	100.34(2)	131.753(7)	93.01(2)	96.37(5)	
γ/°				71.20(2)	
$U/Å^3$	4151(2)	9288(6)	3659(1)	4105(3)	3162(1)
Z	4	8	4	2	4
D_c/g cm^{-3}	1.069	1.680	1.457	1.510	1.547
Scan width/°	1.78 + 0.30 tan θ	0.63 + 0.30 tan θ	1.05 + 0.30 tan θ	1.15 + 0.30 tan θ	1.21 + 0.30 tan θ
$2\theta_{max}$/°	55.1	55.0	55.0	55.0	55.0
No. reflections measured	9921	11 570	8977	19 519	4114
No. reflections used	1876	3215	5069	7920	3781
No. parameters varied	334	488	390	937	353
Data/parameter ratio	5.62	6.59	13.00	8.45	10.71
Transmission factors	0.87–1.00	0.57–1.00	0.76–1.00	0.79–1.00	
Goodness of fit	1.75	1.68	2.74	1.67	2.01
R^a	0.072	0.065	0.057	0.056	0.053
$R'^{a,b}$	0.073	0.060	0.081	0.054	0.063
p Factor[b]	0.030	0.030	0.040	0.030	0.040

[a] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. [b] $w = [\sigma^2(F_o) + \frac{1}{4}p^2(F_o)^2]^{-1}$.

(decomp.) (Found: C, 55.10; H, 5.51; N, 1.53. $C_{37}H_{44}BF_4NRuS_2Ti$ requires C, 55.37; H, 5.53; N, 1.75%); $\tilde{\nu}$/cm^{-1} (NC) 2122m (KBr). Similar reaction of **1b** with $AgPF_6$ in the presence of Bu^{t}NC gave a dark red powder of $[Cp_2Ti(\mu\text{-}SMe)_2Ru(Bu^tNC)Cp^*][PF_6]$ **4b** (75%), m.p. 246.5–250.3 °C (decomp.) (Found: C, 43.72; H, 5.46; N, 1.97. $C_{32}H_{40}F_6NPRuS_2Ti$ requires C, 44.02; H, 5.49; N, 1.90%); $\tilde{\nu}$/cm^{-1} (NC) 2116m (KBr).

$[Cp_2Ti(\mu\text{-}SR)_2Ru(R'CN)Cp^*][PF_6]$ (R = Ph, R′ = Bu^t 5a; R = Me, R′ = Bu^t 5b; R = Ph, R′ = Me 6a; R = R′ = Me 6b). To a mixture of complex **1a** (0.38 g, 0.56 mmol) and $AgPF_6$ (0.15 g, 0.58 mmol) was added thf (15 cm^3). Then Bu^{t}CN (0.080 cm^3, 0.72 mmol) was added immediately, and the solution stirred at room temperature for 9.5 h. It changed from brown to dark red accompanied by precipitation of a dark red powder. The precipitate was filtered off, washed with thf (4 cm^3) and extracted with dichloromethane (10 cm^3). Evaporation of the solvent gave a dark violet powder of $[Cp_2Ti(\mu\text{-}SPh)_2Ru(Bu^tCN)Cp^*][PF_6]$ **5a** (0.37 g, 76%), m.p. 141.0–146.3 °C. Recrystallization from dichloromethane–hexane mixture yielded dark violet needle crystals which contain a dichloromethane molecule (Found: C, 48.15; H, 4.89; N, 1.50. $C_{37}H_{44}F_6NPRuS_2Ti\cdot CH_2Cl_2$ requires C, 48.16; H, 4.89; N, 1.63%). Similar reaction of **1b** with $AgPF_6$ in the presence of Bu^{t}CN gave a dark violet powder of $[Cp_2Ti(\mu\text{-}SMe)_2Ru(Bu^tCN)Cp^*][PF_6]$ **5b** (72%), m.p. 209.7–210.3 °C (Found: C, 44.00; H, 5.49; N, 1.78. $C_{27}H_{40}F_6NPRuS_2Ti$ requires C, 44.02; H, 5.47; N, 1.90%). Similar reaction of **1a** with $AgPF_6$ in the presence of MeCN gave a dark violet powder of $[Cp_2Ti(\mu\text{-}SPh)_2Ru(MeCN)Cp^*][PF_6]$ **6a** (11%), m.p. 116.0–121.5 °C. Recrystallization from dichloromethane–hexane yielded dark violet needle crystals which contain a dichloromethane molecule (Found: C, 46.36; H, 4.47; N, 1.57. $C_{39}H_{38}F_6NPRuS_2Ti\cdot CH_2Cl_2$ requires C, 46.52; H, 4.46; N, 1.55%). Similar reaction of **1b** with $AgPF_6$ in the presence of MeCN gave a dark violet powder of $[Cp_2Ti(\mu\text{-}SMe)_2Ru(MeCN)Cp^*][PF_6]$ **6b** (74%), m.p. 155.0–157.0 °C. Recrystallization from dichloromethane–hexane yielded dark violet needle crystals which contain a dichloromethane molecule (Found: C, 38.78; H, 4.73; N, 1.80. $C_{24}H_{34}F_6NPRuS_2Ti\cdot CH_2Cl_2$ requires C, 38.51; H, 4.66; N, 1.80%).

Crystallography

The crystal data and experimental details for complexes **1a**, **1d**, **4a**, **5a**·CH_2Cl_2 and **5b** are summarized in Table 3. Diffraction data were obtained with a Rigaku AFC-7R diffractometer and Mo-Kα radiation (λ 0.710 69 Å). The reflection intensities were monitored by three standard reflections at every 150 measurements. A decay correction was applied for **1a**. Reflection data were corrected for Lorentz-polarization effects. Absorption corrections were empirically applied for **1a**, **1d**, **4a** and **5a**·CH_2Cl_2, while azimuthal scans of several reflections indicated no need for an absorption correction for **5b**.

The structures were solved by direct methods using SHELXS 86[15] for **1a**, and heavy-atom Patterson methods[16,17] for **1d**, **4a**, **5a**·CH_2Cl_2 and **5b**. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations. All refinements were continued until all shifts were smaller than one-third of the standard deviations of the parameters involved. Atomic scattering factors and anomalous dispersion terms were taken from ref. 18. The positions of the hydrogen atoms were located on idealized positions but not refined. The calculations were performed on an IRIS Indigo computer using the program system TEXSAN.[19]

CCDC reference number 186/1068.

Reaction of 1a or 5a with CO

Complex **1a** (0.046 g, 0.068 mmol) was placed in a flask (30 cm^3). After evacuation, the system was filled with CO (1 atm). Then thf (5 cm^3) was added, and the solution stirred at room temperature for 21 h. It changed from brown to violet. Evaporation of the solvent gave a mixture of $[TiCp_2(SPh)_2]$ and $[RuCl(Cp^*)(CO)_2]$.

The complex **5a**·CH_2Cl_2 (0.068 g, 0.073 mmol) was placed in a flask (20 cm^3). After evacuation, the system was filled with

CO (1 atm). Then dichloromethane (5 cm^3) was added and the solution stirred at room temperature for 24 h. Evaporation of the solvent gave [$Cp_2Ti(\mu\text{-}SPh)_2Ru(CO)Cp^*]^+$. The ^{1}H NMR spectrum showed the same signals as those of **3a**.

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