The Highly Reactive Thiolate-Bridged Diruthenium Complex [Cp*Ru(μ_2-Cl)(μ_2-SPr^i)$_2$RuCp*][OTf]: Its Reactions with Alkynes To Form Dinuclear Metallacycles and Terminal Allenylidene Complexes

Hiroyuki Matsuzaka, Yukihiro Takagi, and Masanobu Hidai*

Department of Synthetic Chemistry, The University of Tokyo, Hongo, Tokyo 113, Japan

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*Summary: Addition of AgOTf (OTf = OSO_2CF_3) to a THF solution of Cp*Ru(Cl)(μ_2-SPr^i)$_2$Ru(Cl)Cp* (1; Cp* = η^5-C_5Me_5) produces [Cp*Ru(μ_2-Cl)(μ_2-SPr^i)$_2$RuCp*] [OTf] (2), which readily reacts with alkynes to form a new set of novel diruthenium complexes in high to excellent yield (Scheme 1). Reaction of 2 with $HC{\equiv}C\overline{C{=}CH(CH_2)_3C}H_2$ (8 equiv) in THF at room temperature results in coupling of the two alkyne molecules at the diruthenium center to form the unique dinuclear metallacycle 3. Similar treatment of 2 with HC≡CR (R = Tol, Ph) induces another type of almost quantitative coupling of the alkyne to afford diruthenacyclopentadienoindane complexes 4 (4a, R′ = Me; 4b, R′ = H). Complex 2 also smoothly reacts with HC≡CC(OH)R_2 (R = Tol, Ph) to give dinuclear terminal allenylidene complexes 6 (6a, R = Tol; 6b, R = Ph). Complexes 3 and 6a have been defined by X-ray crystallography, whereas other compounds were spectroscopically characterized.*

Although organoruthenium complexes containing phosphine ligands have been widely employed in various chemical transformations,[1] the chemistry of organoruthenium complexes with sulfur ligands has been surprisingly unexplored.[2,3] We have recently established general synthetic routes to a series of thiolate-bridged dinuclear Cp*Ru complexes (Cp* = η^5-C_5Me_5),[4,5] which provide bimetallic reaction sites for novel modes of chemical transformation of organic substrates. Thus, reactions of alkynes with Cp*Ru(μ_2-SPr^i)$_2$RuCp* produce dinuclear ruthenacyclopentenyl complexes,[6] whereas those with Cp*Ru(μ_2-SPr^i)$_3$RuCp* yield dinuclear terminal dialkynyl compounds.[7] These observations clearly indicate that reactions of alkynes with the diruthenium–thiolate complexes proceed in quite a different manner, depending upon the nature of the diruthenium site. In this context, we have investigated the reactivity of alkynes with Cp*Ru(Cl)(μ_2-SPr^i)$_2$Ru(Cl)Cp* (1)[4a] and found that complex 1 did not itself react with alkynes; however, addition of AgOTf (OTf = OSO_2CF_3) to 1 produces the highly reactive cationic complex [Cp*Ru(μ_2-Cl)(μ_2-SPr^i)$_2$RuCp*][OTf] (2), which readily incorporates alkynes to give a new set of diruthenium complexes (Scheme 1). As described herein, the chemistry is markedly sensitive to the alkyne employed.

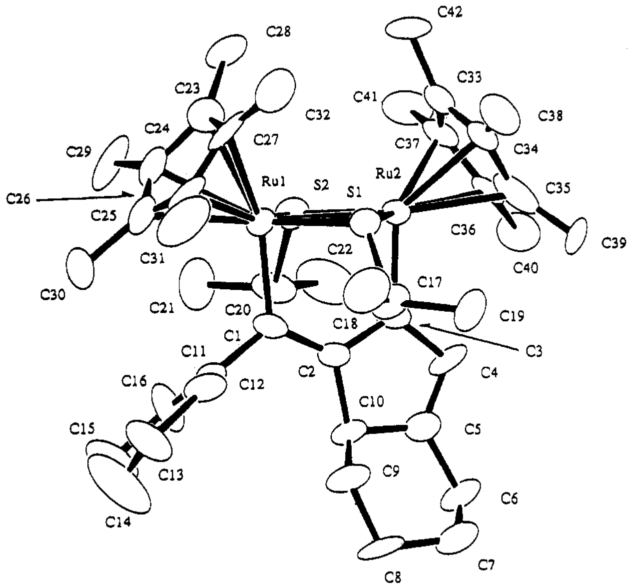

Figure 1. ORTEP drawing of the cationic part of complex 3.

Complex 2 was isolated as a brown crystalline solid and spectroscopically characterized.[8] Its ^{1}H NMR spectrum shows only one set of signals due to Cp* and SPr^i protons, which indicate the triply bridged structure depicted in Scheme 1.

Reaction of 2 with $HC{\equiv}C\overline{C{=}CH(CH_2)_3C}H_2$ (5 equiv) in THF at room temperature results in coupling of the

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(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) (a) Berg, J. M.; Holm, R. H. In *Metal Ions in Biology*; Wiley: New York, 1982; Vol. 4. (b) Rakowski DuBois, M. *Chem. Rev.* **1989**, *89*, 1. (c) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387.

(3) For the pertinent examples, see: (a) Houser, E. J.; Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 7440. (b) Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *J. Chem. Soc., Chem. Commun.* **1989**, 14. (c) Koch, S. A.; Millar, M. *J. Am. Chem. Soc.* **1983**, *105*, 3362. (d) Millar, M. M.; O'Sullivan, T.; Vries, N.; Koch, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 3714. (e) Shaver, A.; Plouffe, P.-Y.; Lilles, D. C.; Singleton, E. *Inorg. Chem.* **1992**, *31*, 997. (f) Kölle, U.; Kang, B.-S.; Englert, U. *J. Organomet. Chem.* **1991**, *420*, 227.

(4) (a) Dev, S.; Imagawa, K.; Mizobe, Y.; Cheng, G.; Wakatsuki, Y.; Yamazaki, H.; Hidai, M. *Organometallics* **1989**, *8*, 1232. (b) Dev, S.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **1990**, *29*, 4797. (c) Takahashi, A.; Mizobe, Y.; Matsuzaka, H.; Dev, S.; Hidai, M. *J. Organomet. Chem.* **1993**, *456*, 243.

(5) Some dinuclear CpRu and Cp*Ru complexes have been recently reported. See: (a) Rauchfuss, T. B.; Rodgers, D. P. S.; Wilson, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 3114. (b) Loren, S. D.; Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Bursten, B. E.; Luth, K. W. *J. Am. Chem. Soc.* **1989**, *111*, 4712. (c) Knox, S. A. R. *J. Organomet. Chem.* **1990**, *400*, 255 and references cited therein. (d) Kölle, U.; Kang, B.-S.; Thewalt, U. *Organometallics* **1992**, *11*, 2893. (e) Suzuki, H.; Takao, T.; Tanaka, M.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 476.

(6) Nishio, M.; Matsuzaka, H.; Mizobe, Y.; Hidai, M. *J. Chem. Soc., Chem. Commun.* **1993**, 375.

(7) Matsuzaka, H.; Hirayama, Y.; Nishio, M.; Mizobe, Y.; Hidai, M. *Organometallics* **1993**, *12*, 36.

(8) A brown suspension of Cp*Ru(Cl)(μ_2-SPr^i)$_2$Ru(Cl)Cp* (1; 850 mg, 1.22 mmol) in THF (20 mL) immediately turned to a reddish brown solution when a THF (2 mL) solution of AgOTf (312 mg, 1.22 mmol) was added. The reaction mixture was stirred overnight at room temperature. After removal of the solvent, the resultant solid was extracted with CH_2Cl_2. Addition of hexane to the concentrated CH_2Cl_2 solution afforded 2 as a dark brown crystalline solid, yield 92%. ^{1}H NMR ($CDCl_3$): δ 4.05 (sep, 2H, J = 6.7 Hz, SC*H*Me$_2$), 1.64 (s, 30H, Cp*), 1.52 (d, 12H, J = 6.7 Hz, SCH*Me*$_2$).

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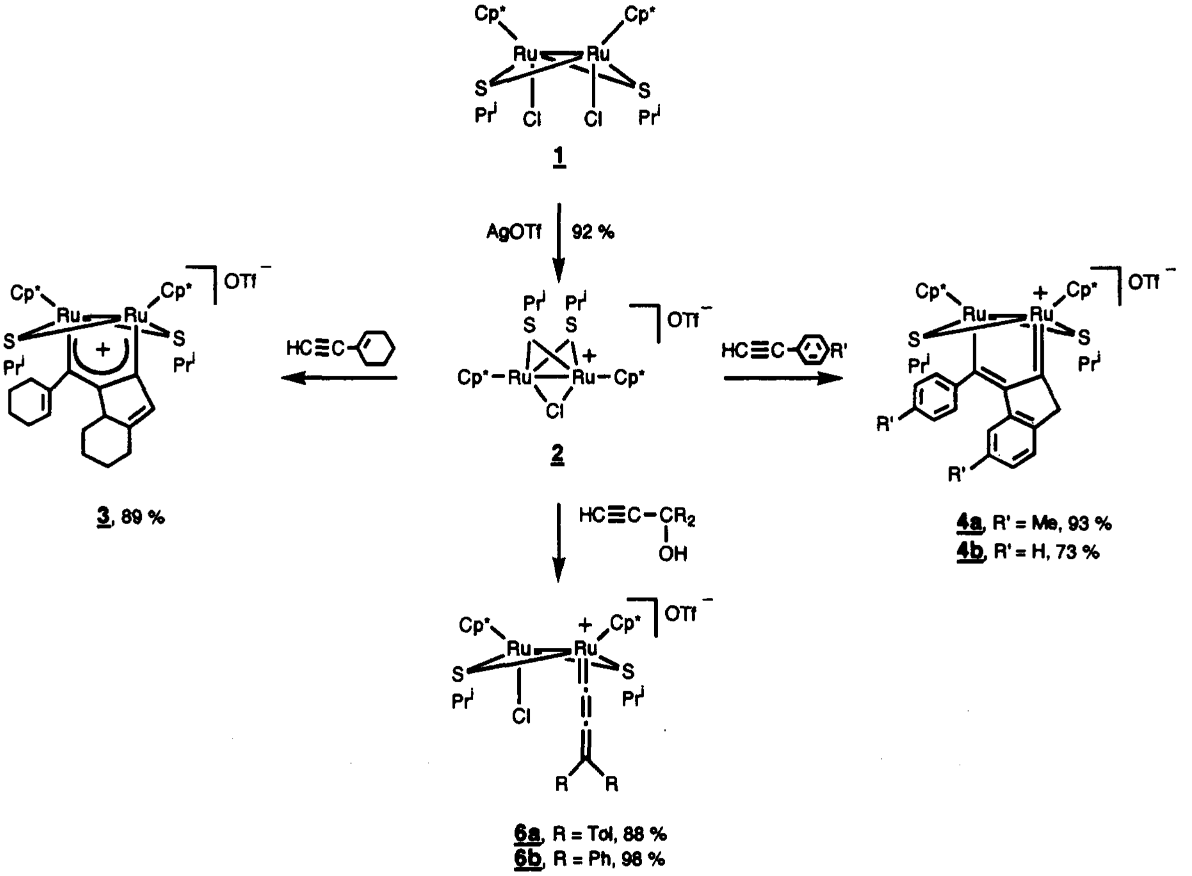
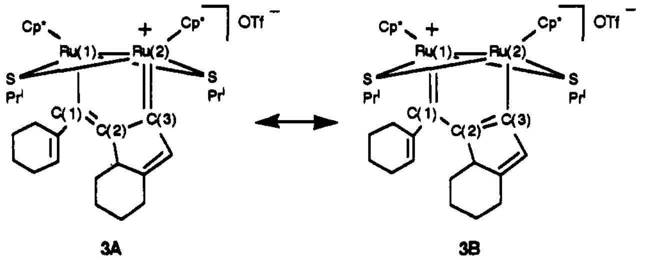
Scheme 1

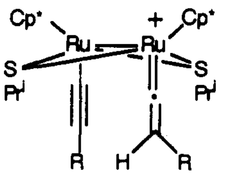


two alkyne molecules at the diruthenium center to form the unique dinuclear metallacycle 3 in high yield, which was isolated as a green microcrystalline solid[9] and fully characterized by X-ray crystallography[10] (Figure 1). Two $HC{\equiv}C\overline{C{=}CH(CH_2)_3C}H_2$ molecules form a fused-ring system with Ru(1) and Ru(2). The five-membered metallacycle is essentially planar and appears to be best described as a hybrid of the two resonance forms 3A and 3B, considering bond distances.[10]

Similar treatment of 2 with HC≡CR (R = Tol, Ph) induces another type of almost quantitative coupling of the alkyne to afford diruthenacyclopentadienoindane complexes 4 (4a, R′ = Me; 4b, R′ = H),[11] which have been spectroscopically characterized. Previously complexes 4 were alternatively obtained by protonation of dialkynyl complexes $Cp^*Ru(C{\equiv}CR)(\mu_2\text{-}SPr^i)_2Ru(C{\equiv}CR)Cp^*$ (5: 5a, R = Tol; 5b, R = Ph) and crystallographically defined.[7]



It is interesting to note that HC≡CR (R = Tol, Ph) directly coupled on the diruthenium site in 2 to produce 4 in high yield. Extremely high reactivity of 2 toward alkynes is also demonstrated by instant formation of 3, which could not be obtained by protonation of the corresponding dialkynyl complex 5c (R = $\overline{C{=}CH(CH_2)_3C}H_2$).[7] The unique chemical transformation of these terminal alkynes at the diruthenium center to afford complexes 3 and 4 is considered to proceed via vinylidene–alkynyl intermediates such as 7, which was proposed for the coupling of two terminal alkynyl moieties in 5.[7]



7

R = cyclohexenyl
Tol, Ph

Complex 2 also smoothly reacts with $HC{\equiv}CC(OH)R_2$ (R = Tol, Ph) to give dinuclear terminal allenylidene

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[9] *To a reddish brown THF (10 mL) solution of 2 (64 mg, 0.079 mmol)* was added $HC{\equiv}C\overline{C{=}CH(CH_2)_3C}H_2$ (74 μL, 0.63 mmol), and the reaction mixture was stirred overnight at room temperature. After removal of the solvent, the resultant solid was washed with hexane (5 mL × 3) and chromatographed on alumina with CH_2Cl_2. Evaporation of the solvent from a green band gave 3 as a microcrystalline solid (69 mg, 89%). Single crystals suitable for structural analysis were obtained by recrystallization from THF–ether. ^1H NMR ($CDCl_3$, methylene protons are omitted): δ 6.96 (s, 1H, vinyl), 4.61 (br s, 1H, vinyl), 3.45, 2.64 (sep, 1H each, J = 6.8 Hz, SC*H*Me$_2$), 1.85, 1.69 (s, 15H each, Cp*), 1.40, 1.25, 0.95, 0.82 (d, 3H each, J = 6.8 Hz, SCH*Me*$_2$).

[10] Crystal data: $P\bar{1}$ (triclinic), a = 12.552(3) Å, b = 16.310(4) Å, c = 11.019(2) Å, α = 94.72(2)°, β = 100.96(1)°, γ = 88.33(2)°, V = 2206.9(8) Å^3, Z = 2, R (R_w) = 6.3% (5.2%) for 5272 reflections ($I > 3\sigma(I)$). Bond distances (Å) and angles (deg): Ru(1)–Ru(2), 2.777(1); Ru(1)–C(1), 2.06(1); Ru(2)–C(3), 2.04(1); C(1)–C(2), 1.44(1); C(2)–C(3), 1.42(1); Ru(2)–Ru(1)–C(1), 87.1(3); Ru(1)–Ru(2)–C(3), 85.9(3); Ru(1)–C(1)–C(2), 120.1(8); C(1)–C(2)–C(3), 124(1); Ru(2)–C(3)–C(2), 122.7(9).

[11] Complexes 4 were obtained by analogous treatment of 2 with HC≡CR (R = Tol, Ph): 4a, yield 93%; 4b, yield 73%.

complexes **6** (**6a**, R = Tol; **6b**, R = Ph) in excellent yield, which were obtained as violet crystalline solids and spectroscopically characterized;[12] **6a** was further defined by X-ray crystallography[13] (Figure 2). The η^1-allenylidene and Cl ligands are on different Ru atoms in a mutually *cis* configuration. Complex **6** offers a rare example of a multinuclear allenylidene compound with only a terminal allenylidene ligand on the bimetallic center.[14]

Finally, it should be mentioned that transformations of alkynes described above proceed without isolating **2**. Thus, addition of alkyne to a mixture of **1** and AgOTf in THF results in clean formation of **3**, **4**, and **6**, respectively. These cationic complexes would have a rich chemistry with organic and inorganic nucleophilic substrates, and further studies are in progress toward this direction.

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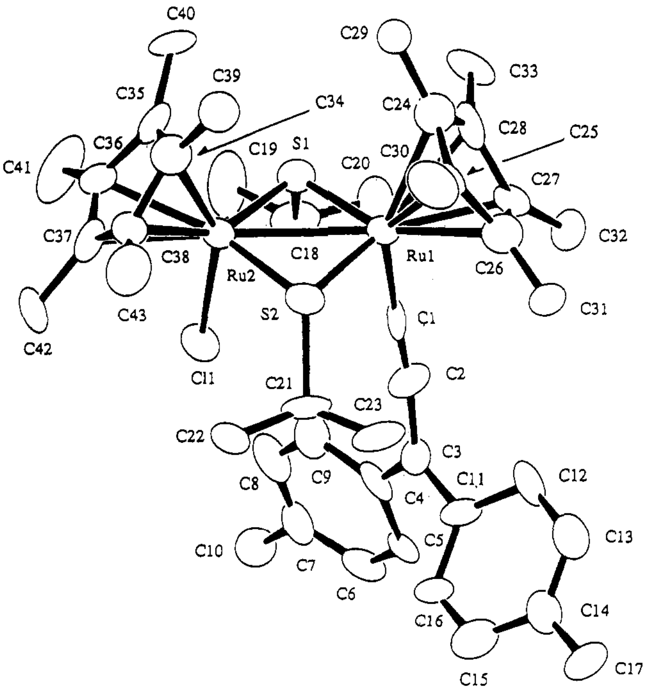

Figure 2. ORTEP drawing of the cationic part of complex **6a**.

Supplementary Material Available: Text giving experimental details, including results of elemental analysis, and for **3** and **6a**, tables of positional parameters, anisotropic thermal parameters, and bond distances and angles (16 pages). Ordering information is given on any current masthead page.

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[12] A THF (20 mL) solution of **2** (578 mg, 0.716 mmol) immediately turned to dark violet when a THF (5 mL) solution of $HC{\equiv}CC(OH)Tol_2$ (177 mg, 0.749 mmol) was added, and the reaction mixture was stirred overnight at room temperature. After removal of the solvent, the resultant solid was washed with hexane (5 mL × 3) and chromatographed on silica gel with THF. Evaporation of the solvent from a violet band gave **6a** as a microcrystalline solid (650 mg, 88%). Single crystals suitable for structural analysis were obtained by recrystallization from ethanol/hexane. **6a**: yield 88%. ^{1}H NMR ($CDCl_3$): δ 7.57, 7.20 (d, 4H each, J = 8.1 Hz, aryl), 4.31 (sep, 2H, J = 6.8 Hz, SC*H*Me$_2$), 2.36 (s, 6H, C_6H_4*Me*), 1.85, 1.67 (s, 15H each, Cp*), 1.32, 1.20 (d, 6H each, J = 6.8 Hz, SCH*Me*$_2$). IR (KBr): $\nu_{C=C=C}$ 1941 cm^{-1}. **6b**: yield 98%. ^{1}H NMR ($CDCl_3$): δ 7.62–7.05 (m, 10H, aryl), 4.46 (sep, 2H, J = 6.8 Hz, SC*H*Me$_2$), 1.85, 1.44 (s, 15H each, Cp*), 1.26, 1.12 (d, 6H each, J = 6.8 Hz, SCH*Me*$_2$). IR (KBr): $\nu_{C=C=C}$ 1933 cm^{-1}.

[13] Crystal data: $P2_1/c$ (monoclinic), a = 10.090(3) Å, b = 23.067(6) Å, c = 19.529(2) Å, β = 92.75(1)°, V = 4540(1) Å^3, Z = 4, R (R_w) = 9.2% (6.7%) for 4115 reflections ($I > 3\sigma(I)$). Bond distances (Å) and angles (deg): Ru(1)–Ru(2), 2.801(2); Ru(1)–C(1), 1.94(2); Ru(2)–Cl(1), 2.414(5); C(1)–C(2), 1.24(2); C(2)–C(3), 1.36(2); Ru(2)–Ru(1)–C(1), 97.4(5); Ru(1)–Ru(2)–Cl(1), 96.4(1); Ru(1)–C(1)–C(2), 174(1); C(1)–C(2)–C(3), 165(2)°.

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