Remarkable Effect of Halogens on Catalytic Activities of Thiolato-Bridged Diruthenium Complexes in Propargylic Substitution Reactions

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Thiolato-bridged dibromo- and diiododiruthenium complexes [{Cp*RuX(μ-SR)}$_2$] (X = Br, I; R = Me, ^{i}Pr) have been prepared and characterized by X-ray analysis. Examination of their catalytic activity in propargylic substitution reactions of 1-phenyl-2-propyn-1-ol with some nucleophiles has revealed that the complexes [{Cp*RuX(μ-S^{i}Pr)}$_2$] (X = Br, I) work as catalysts but less effectively in comparison with the well-investigated dichloride analogue [{Cp*RuCl(μ-S^{i}Pr)}$_2$].

Introduction

We have previously demonstrated that thiolato-bridged dichlorodiruthenium complexes [Cp*RuCl(μ-SR)]$_2$ (R = Me (**1a**), ^{i}Pr (**1b**), etc; Cp* = η^5- C_5Me_5) efficiently catalyze propargylic substitution reactions of propargylic alcohols with a variety of carbon- and heteroatom-centered nucleophiles to afford the corresponding functionalized propargylic compounds (Scheme 1).[1] Furthermore, we have developed some enantioselective versions of these catalytic reactions.[1,2] Stoichiometric and theoretical studies have revealed that the cationic allenylidene species (**A**) generated by the reaction of the thiolato-bridged dichlorodiruthenium complex with a propargylic alcohol is an actual intermediate and the propargylic substitution reaction proceeds via nucleophilic attack of a nucleophile on the electrophilic C_γ atom of this species.[3−5]

Investigation on the catalytic reactivity of a series of chalogenolato-bridged diruthenium complexes [{Cp*RuCl(μ-YR)}$_2$] (Y = S, Se, Te), where electronic properties of two ruthenium atoms are modulated directly by the bridging chalcogen atoms, has also suggested that the possible charge transfer between two ruthenium atoms (synergistic effect) is one of the key factors for the catalytic reactions.[6,7] On the other hand, the catalytic activity of analogous thiolato-bridged diruthenium complexes having other halide ligands than chloride such as bromide and iodide [{Cp*RuX(μ-SR)}$_2$] (X = Br, I) has not yet been investigated, although halide ligands coordinated to the ruthenium atoms are expected to affect the electronic properties of the diruthenium core as well as the formation of the cationic allenylidene complex which is generated by removal of halogen atoms from the ruthenium atom and by subsequent coordination of a propargylic alcohol to it. As an extension of our chemistry, we have now prepared a series of thiolato-bridged dibromo- and diiododiruthenium complexes [{Cp*RuX(μ-SR)}$_2$] (**2a**: R = Me, X = Br; **2b**: R = ^{i}Pr, X = Br; **3a**: R = Me, X = I; **3b**: R = ^{i}Pr, X = I) (Chart 1) and investigated their catalytic activity in propargylic substitution reactions.

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(2) Enantioselective catalytic propargylic substitution reactions have been recently developed for Cu and Ni catalysts: (a) Detz, R. J.; Delville, M. M. E.; Hiemstra, H.; van Maarseveen, J. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 3777. (b) Hattori, G.; Matsuzawa, H.; Miyake, Y.; Nishibayashi, Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 3781. (c) Smith, S. W.; Fu, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 12645.

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(4) For recent examples of catalytic reactions via allenylidene complexes as key intermediates by our groups, see: (a) Fukamizu, K.; Miyake, Y.; Nishibayashi, Y. *J. Am. Chem. Soc.* **2008**, *130*, 10498. (b) Yada, Y.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2008**, *27*, 3614. (c) Daini, M.; Yoshikawa, M.; Inada, Y.; Uemura, S.; Sakata, K.; Kanao, K.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2008**, *27*, 2046. (d) Yamauchi, Y.; Yuki, M.; Tanabe, Y.; Miyake, Y.; Inada, Y.; Uemura, S.; Nishibayashi, Y. *J. Am. Chem. Soc.* **2008**, *130*, 2908. (e) Matsuzawa, H.; Kanao, K.; Miyake, Y.; Nishibayashi, Y. *Org. Lett.* **2007**, *9*, 5561. (f) Matsuzawa, H.; Miyake, Y.; Nishibayashi, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 6488. (g) Yamauchi, Y.; Onodera, G.; Sakata, K.; Yuki, M.; Miyake, Y.; Uemura, S.; Nishibayashi, Y. *J. Am. Chem. Soc.* **2007**, *129*, 5175. (h) Inada, Y.; Yoshikawa, M.; Milton, M. D.; Nishibayashi, Y.; Uemura, S. *Eur. J. Org. Chem.* **2006**, 881. (i) Onodera, G.; Nishibayashi, Y.; Uemura, S. *Organometallics* **2006**, *25*, 35. (j) Nishibayashi, Y.; Uemura, S. *Curr. Org. Chem.* **2006**, *10*, 135, and references therein.

(5) For recent examples of catalytic reactions via allenylidene complexes as key intermediates, see: (a) Yeh, K.-L.; Liu, B.; Lo, C.-Y.; Huang, H.-L.; Liu, R.-S. *J. Am. Chem. Soc.* **2002**, *124*, 6510. (b) Datta, S.; Chang, C.-L.; Yeh, K.-L.; Liu, R.-S. *J. Am. Chem. Soc.* **2003**, *125*, 9294. (c) Shen, H.-C.; Su, H.-L.; Hsueh, Y.-C.; Liu, R.-S. *Organometallics* **2004**, *23*, 4332. (d) Cadierno, V.; García-Garrido, S. E.; Gimeno, J. *Adv. Synth. Catal.* **2006**, *348*, 101. (e) Liu, R.-S. *Synlett* **2008**, 801, and references therein.

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(7) Phosphido-bridged diruthenium complexes also catalyze propargylic substitution reactions, see: (a) Miyake, Y.; Endo, S.; Nomaguchi, Y.; Yuki, M.; Nishibayashi, Y. *Organometallics* **2008**, *27*, 4017. (b) Miyake, Y.; Endo, S.; Yuki, M.; Tanabe, Y.; Nishibayashi, Y. *Organometallics* **2008**, *27*, 6039.

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Scheme 1

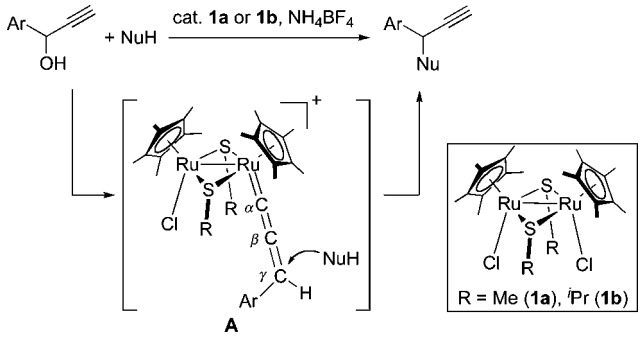
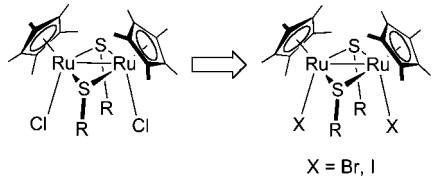
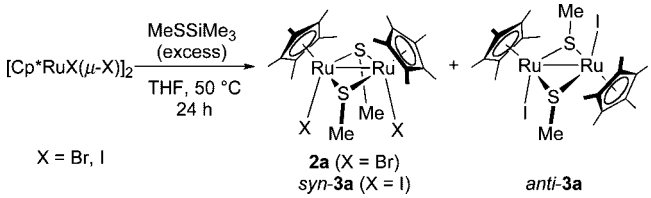


Chart 1



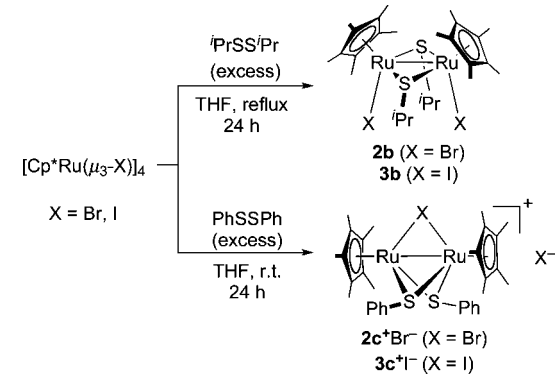
Scheme 2



Results and Discussion

Halide-substituted complexes [{Cp*RuX(μ-SR)}$_2$] (X = Br, I) can be prepared in a similar way as that for the preparation of **1a** and **1b**.[6,8] When tetrabromodiruthenium(III) complex [{Cp*RuBr(μ-Br)}$_2$] was heated with an excess amount of trimethyl(methylthio)silane in THF (tetrahydrofuran) at 50 °C, the methanethiolato-bridged dibromodiruthenium complex (**2a**) was obtained in 59% yield (Scheme 2). The ^{1}H NMR spectra of the crude product as well as the preliminary X-ray analysis of **2a** clearly indicated that **2a** is obtained as a sole product where the two bromides or Cp* ligands are located at the position *cis* to one another.[9] On the other hand, the reaction of the tetraiododiruthenium(III) complex [{Cp*RuI(μ-I)}$_2$] with an excess amount of trimethyl(methylthio)silane in THF at 50 °C afforded the methanethiolato-bridged diiododiruthenium complex (**3a**) as a mixture of *syn* and *anti* isomers in 73% yield with a ratio of 4:1 after recrystallization from dichloromethane-*n*-hexane (Scheme 2). The formation of such two stereoisomers has been reported in the preparation of chalcogenolato-bridged diruthenium complexes [{Cp*RuCl(μ-YR)}] (Y = S, Se, Te), the *syn* and *anti* ratio being dependent on the kind of organic groups R on the chalcogen atoms.[6b] A preliminary X-ray analysis of the major isomer of **3a** reveals that *syn*-**3a** is dominantly generated.[9]

Scheme 3



Treatment of bromo- and iodo-bridged tetraruthenium(II) complex [{Cp*Ru(μ_3-X)}$_4$] (X = Br, I) with an excess amount of diisopropyl disulfide in THF at reflux temperature for 24 h afforded the corresponding 2-propanethiolato-bridged dibromo- and diiododiruthenium complexes (**2b** and **3b**) in 53% and 50% yield, respectively (Scheme 3). Both **2b** and **3b** were previously prepared either by thermal decomposition of the benzyl complex [{Cp*Ru(μ-S^{i}Pr)}$_2$Br(CH$_2$Ph)][10] or by substitution reaction of the diacetylido complex [{Cp*Ru(CCR)(μ-S^{i}Pr)}$_2$] (R = Ph, Tol) with I$_2$.[11] However, the reaction of the tetraruthenium(II) complexes with diisopropyl disulfide provides a more convenient method for the preparation of **2b** and **3b**. The ^{1}H and ^{13}C NMR spectra of **2b** and **3b** indicated that only *syn* isomers were produced, respectively, and the detailed structure of **2b** and **3b** was determined by X-ray analysis (Figure 1). The molecular structure of **1b**[6,8] is also shown in Figure S1 in Supporting Information. The crystallographic study of **1b**, **2b**·CH$_2$Cl$_2$ and **3b** has figured out that there is no significant difference among the structures of **1b**, **2b** and **3b** except for the expected Ru-halogen bond distances in order of **3b** > **2b** > **1b** (see figure captions in Figure 1).[12]

Similar reactions of [{Cp*Ru(μ_3-X)}$_4$] (X = Br, I) with an excess amount of diphenyl disulfide in THF at room temperature for 24 h gave the cationic bis(benzenethiolato)(bromo)-bridged

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(9) Preliminary crystallographic data for **2a**: $C_{22}H_{36}Br_2Ru_2S_2$, orthorhombic, space group *Fdd*2, a = 36.420(9) Å, b = 8.716(2) Å, c = 16.202(5) Å, V = 5143(2) Å^3, Z = 8. Preliminary crystallographic data for *syn*-**3a**: $C_{22}H_{36}I_2Ru_2S_2$, orthorhombic, space group *Fdd*2, a = 36.7734(12) Å, b = 8.6494(2) Å, c = 16.5805(5) Å, V = 5273.7(3) Å^3, Z = 8. Both isomorphous structures could not be refined critically because of the existence of disorders among Cp* carbons.

(10) (a) Takahashi, A.; Mizobe, Y.; Matsuzaka, H.; Dev, S.; Hidai, M. *J. Organomet. Chem.* **1993**, *456*, 243. (b) Takahashi, A.; Mizobe, Y.; Hidai, M. *Chem. Lett.* **1994**, 371.

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(12) Crystallographic data for **1b**: $C_{26}H_{44}Cl_2Ru_2S_2$, FW = 693.80, monoclinic, space group *C*2/*c*, a = 20.8897(9) Å, b = 8.6800(3) Å, c = 18.0832(9) Å, β = 122.0497(10)°, V = 2779.2(2) Å^3, Z = 4, d_{calcd} = 1.658 g cm^{-3}, μ = 14.432 cm^{-1}, *R*1 (*wR*2) = 0.0297 (0.0651) for 185 variants and 3180 unique reflections. Crystallographic data for **2b**·CH$_2$Cl$_2$: $C_{27}H_{46}Br_2Cl_2Ru_2S_2$, FW = 867.63, monoclinic, space group $P2_1/n$, a = 10.3998(8) Å, b = 30.766(2) Å, c = 10.4445(12) Å, β = 77.749(3)°, V = 3265.8(5) Å^3, Z = 4, d_{calcd} = 1.765 g cm^{-3}, μ = 36.867 cm^{-1}, *R*1 (*wR*2) = 0.0694 (0.1472) for 363 variants and 7436 unique reflections. Crystallographic data for **3b**: $C_{26}H_{44}I_2Ru_2S_2$, FW = 876.70, monoclinic, space group $P2_1/c$, a = 10.9054(3) Å, b = 15.2797(4) Å, c = 18.1994(5) Å, β = 89.5676(9)°, V = 3032.50(14) Å^3, Z = 4, d_{calcd} = 1.920 g cm^{-3}, μ = 31.841 cm^{-1}, *R*1 (*wR*2) = 0.0391 (0.0531) for 339 variants and 6909 unique reflections. Crystallographic data for **2c**$^+$Br$^-$·CH$_2$Cl$_2$: $C_{32}H_{46}Br_2Cl_2Ru_2S_2$, FW = 935.67, orthorhombic, space group *Pnma*, a = 15.9650(5) Å, b = 13.2040(3) Å, c = 17.0513(4) Å, V = 3594.45(16) Å^3, Z = 4, d_{calcd} = 1.729 g cm^{-3}, μ = 33.570 cm^{-1}, *R*1 (*wR*2) = 0.0523 (0.1433) for 252 variants and 4225 unique reflections. Crystallographic data for **3c**$^+$I$^-$: $C_{32}H_{40}I_2Ru_2S_2$, FW = 944.74, orthorhombic, space group *Pnma*, a = 16.5732(4) Å, b = 14.4347(5) Å, c = 14.0403(3) Å, V = 3358.85(16) Å^3, Z = 4, d_{calcd} = 1.868 g cm^{-3}, μ = 28.826 cm^{-1}, *R*1 (*wR*2) = 0.0287 (0.0543) for 209 variants and 3982 unique reflections. See Supporting Information for crystallographic details.

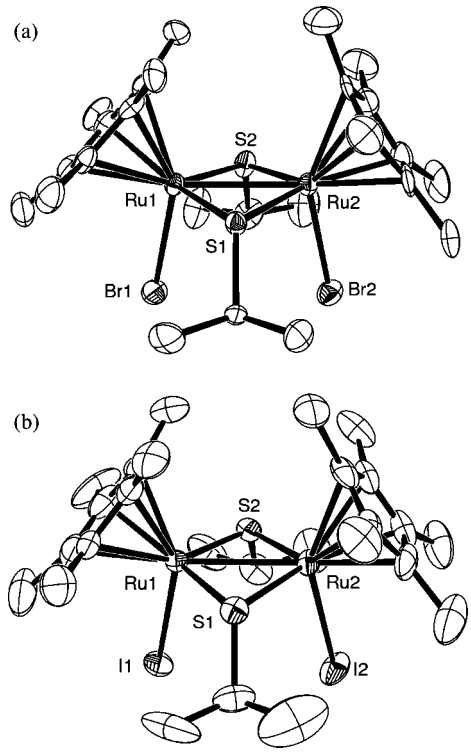


Figure 1. Crystal structures of (a) **2b** and (b) **3b**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) for **2b** (values without SEs in parentheses are averaged): Ru(1)−Ru(2), 2.8329(9); Ru−Br, 2.561; Ru−S, 2.314; Ru−Ru−S, 52.2; S−Ru−S, 103.8; Ru(1)−S−Ru(2), 75.5. For **3b**: Ru(1)−Ru(2), 2.8504(4); I−Ru, 2.731; Ru−S, 2.318; Ru−Ru−S, 52.1; S(1)−Ru−S(2), 103.6; Ru(1)−S−Ru(2), 75.9. For **1b** (see Figure S1 in Supporting Information): Ru(1)−Ru(1)*, 2.8329(2); Ru(1)−Cl(1), 2.4125(9); Ru(1)−S(1), 2.313; Ru(1)*−Ru(1)−S(1), 52.2; S(1)−Ru(1)−S(1)*, 103.44(2); Ru(1)−S(1)−Ru(1)*, 75.53(3).

diruthenium complex [{Cp*Ru(μ-SPh)}$_2$(μ-Br)]Br (**2c**$^+$Br$^-$) and the cationic bis(benzenethiolato)(iodo)-bridged diruthenium complex [{Cp*Ru(μ-SPh)}$_2$(μ-I)]I (**3c**$^+$I$^-$) in 26% and 37% yields, respectively (Scheme 3). The crystallographic study of **2c**$^+$Br$^-$·CH_2Cl_2 and **3c**$^+$I$^-$ clarifies that one halide anion is removed from the diruthenium core to form the cationic species, while the other halide bridges two ruthenium atoms as depicted in Figure 2. Comparison among the structures of [{Cp*Ru(μ-SPh)}$_2$(μ-Cl)] (**1c**$^+$),[6b] **2c**$^+$ and **3c**$^+$ also asserts that there are less distinctions (e.g., Ru−Ru bond distances of **2c**$^+$ and **3c**$^+$ are about the same with that of **1c**$^+$ (2.6879(4) Å))[6b] except for the Ru-halogen bond distances in order of **3c**$^+$ > **2c**$^+$ > **1c**$^+$ (**1c**$^+$: 2.517 Å (mean);[6b] see figure captions in Figure 2).[12]

Next, we examined the catalytic activity of the 2-propanethiolato-bridged diruthenium complexes **1b**, **2b**, and **3b** in propargylic substitution reactions of 1-phenyl-2-propyn-1-ol with a variety of carbon- and heteroatom-centered nucleophiles. Typical results are shown in Table 1. All reactions were carried out in the presence of 2.5 mol% catalyst (**1b**, **2b**, or **3b**) and 5 mol% NH_4BF_4 (Scheme 4) with acetone (Table 1, runs 1−3), 2-methylfuran (Table 1, runs 4−6), aniline (Table 1, runs 7−9), and ethanol (Table 1, runs 10−12) as nucleophiles, which were known to be good reactants against propargylic alcohols when **1a** and **1b** were used as catalysts.[1,4,6] The obtained results obviously indicate that the thiolato-bridged dibromo- and diiododiruthenium complexes **2b** and **3b** work as catalysts but less effectively in propargylic substitution reactions in comparison with the well-investigated thiolato-bridged dichlorodiruthenium complex **1b**. The order of their catalytic activity was revealed to be **1b** > **2b** > **3b**.

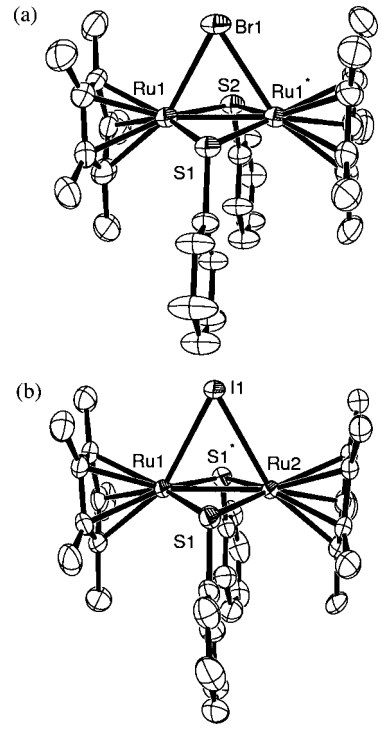
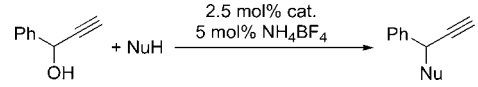


Figure 2. Crystallographic structures of (a) **2c**$^+$ and (b) **3c**$^+$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) for **2c**$^+$ (values without SEs in parentheses are averaged): Ru(1)−Ru(1)*, 2.6923(7); Ru(1)−Br(1), 2.6759(10); Ru(1)−S, 2.322; Ru(1)*-Ru(1)−Br(1), 59.797(19); Ru(1)*−Ru(1)−S, 54.6;Br(1)−Ru(1)−S,77.2;S(1)−Ru(1)−S(2),108.33(6);Ru(1)−Br(1)−Ru(1)*, 60.41(2); Ru(1)−S−Ru(1)*, 70.9. For **3c**$^+$: Ru(1)−Ru(2), 2.6796(5); I(1)−Ru, 2.848; Ru−S(1), 2.322; I(1)−Ru−Ru, 61.9; Ru−Ru−S(1), 54.8;I(1)−Ru−S(1),78.2;S(1)−Ru−S(1)*,108.8;Ru(1)−I(1)−Ru(2), 56.120(13); Ru(1)−S(1)−Ru(2), 70.49(3).

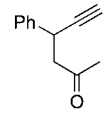
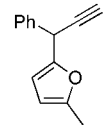
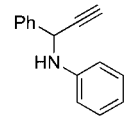
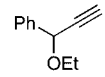
Scheme 4



This remarkable effect of halides on the catalytic activity may highly associate with the significant difference in redox behaviors observed for **1b**, **2b** and **3b** by cyclic voltammetric study. Cyclic voltammogram of **1b** exhibited two sequential one-electron reversible oxidation waves at $E_{1/2}$ = +0.19 and +1.16 V vs Fc/Fc$^+$ (Fc = ferrocene). Similar waves were previously observed for **1a** ($E_{1/2}$ = −0.04, and +0.89 V).[7a] Stepwise oxidation as well as a stable core structure tolerant against oxidation seems to contribute to the high catalytic activity of **1a** and **1b**, where the synergistic dimetallic effect of the core is proposed to be one of the key factors of catalytic cycle.[1,4] On the other hand, three irreversible oxidation waves (+0.19, +0.70, +1.11 V) and five irreversible oxidation waves (+0.13, +0.39, +0.65, +0.89, +1.16 V) were observed for **2b** and **3b**, respectively, showing that the core structure of **2b** and **3b** is unstable and some oxidized species other than the catalytic active species may be easily formed by oxidation.

In summary, we have prepared a series of halide-substituted thiolato-bridged diruthenium complexes [{Cp*RuX(SR)}$_2$] (R = Me, ^{i}Pr; X = Br, I) and demonstrated that thiolato-bridged dibromo- or diiododiruthenium complexes work as catalysts but

Table 1. Ruthenium-Catalyzed Reactions of 1-Phenyl-2-propyn-1-ol with Nucleophiles[a]

run	nucleophile	cat.	solvent	temp (°C)	time (h)	product	yield (%)[b]
1		**1b**					60
2	acetone	**2b**	acetone (12 mL)	reflux	2		47
3		**3b**					4
4[c]		**1b**					56
5[c]		**2b**	$ClCH_2CH_2Cl$ (10 mL)	60	1		53
6[c]	(4.0 mmol)	**3b**					36
7		**1b**					63
8		**2b**	$ClCH_2CH_2Cl$ (18 mL)	60	1		52
9	(3.0 mmol)	**3b**					24
10		**1b**					84
11	EtOH	**2b**	$ClCH_2CH_2Cl$ (14 mL)/ EtOH (1 mL)	60	1		75
12		**3b**					61

[a] Reactions were carried out using 1-phenyl-2-propyn-1-ol (0.60 mmol) in the presence of a catalyst (0.015 mmol) and NH_4BF_4 (0.030 mmol). [b] Isolated yield. [c] Reactions were carried out using 1-phenyl-2-propyn-1-ol (0.40 mmol) in the presence of a catalyst (0.010 mmol) and NH_4BF_4 (0.020 mmol).

less effectively in comparison with the well-investigated dichloride analogue. These results imply that the catalytic activity of diruthenium complexes is controlled not only by nature of bridging heteroatom ligands[6] but also by halide ligands[13] coordinated to the ruthenium atoms, and also indicate that the introduction of appropriate ligands other than chlorides onto the diruthenium core may regulate the synergistic effect of the diruthenium core and may improve the catalytic activity. Further investigations including the preparation of more active catalysts are now in progress.

Experimental Section

General Methods. All manipulations were carried out under an atmosphere of dry dinitrogen using standard Schlenk techniques unless otherwise specified. All solvents were dried by common procedures and degassed before use. $[\{Cp^*RuCl(\mu\text{-}Cl)\}_2]$,[14] $[\{Cp^*RuX(\mu\text{-}X)\}_2]$ (X = Br, I),[15] $[\{Cp^*Ru(\mu_3\text{-}X)\}_4]$ (X = Cl, I),[16] and **1b**[6,8] were prepared according to the literature methods; $[\{Cp^*Ru(\mu_3\text{-}Br)\}_4]$ was prepared in a similar way as that described for the preparation of $[\{Cp^*Ru(\mu_3\text{-}I)_4\}]$;[16] all other reagents were obtained from commercial sources and used without further purification. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL Excalibur 270 spectrometer (^1H, 270 MHz; ^{13}C, 67.8 MHz) using $CDCl_3$ as solvent at room temperature. Elemental analyses were performed at the Microanalytical Center of The University of Tokyo. Oxidation potentials were measured on an ALS model 610C electrochemical analyzer by cyclic voltammetry (Pt working electrode, scan rate 100 mV/s) in dichloromethane containing 0.1 M $^nBu_4NClO_4$ and 5 mM sample at 25 °C. X-ray diffraction data for **1b**, **2b**·CH_2Cl_2, **3b**, **2c**$^+Br^-$·CH_2Cl_2 and **3c**$^+I^-$, summarized in Supporting Information, were collected at −100 °C on a Rigaku RAXIS RAPID imaging plate area detector with graphite-monochromated Mo K_α radiation (λ = 0.7107 Å).

Preparation of 2a. To a suspension of $[\{Cp^*RuBr(\mu\text{-}Br)\}_2]$ (57.2 mg, 0.072 mmol) in THF (5 mL) was added trimethyl(methylthio)silane (0.2 mL, 1.4 mmol), and the mixture was stirred at 50 °C for 24 h. After removal of the solvent, the residue was extracted with dichloromethane. Recrystallization from dichloromethane-*n*-hexane afforded reddish purple plate crystals of **2a** (31.2 mg, 0.043 mmol, 59%). ^1H NMR (δ): 1.68 (s, 30H, Cp*), 2.94 (s, 6H, SMe). Anal. Calcd for $C_{22}H_{36}Br_2Ru_2S_2$: C, 36.37; H, 4.99. Found: C, 36.34; H, 5.18.

Preparation of *syn*-3a. To a suspension of $[\{Cp^*RuI(\mu\text{-}I)\}_2]$ (120.9 mg, 0.123 mmol) in THF (5 mL) was added trimethyl(methylthio)silane (0.4 mL, 2.8 mmol), and the mixture was stirred at 50 °C for 24 h. After removal of the solvent, the residue was extracted with dichloromethane. Recrystallization from dichloromethane-*n*-hexane afforded a mixture of *syn*-**3a** and *anti*-**3a** (74.2 mg, 0.090 mmol, 73%) as reddish purple plate crystals and a red powder, respectively. Pure sample of *syn*-**3a** (11.6 mg, 0.0014 mmol, 11%) was isolated by collecting plate crystals with the help of a microscope. *syn*-**3a**: ^1H NMR (δ): 1.79 (s, 30H, Cp*), 3.58 (br, 6H, SMe). $^{13}C\{^1H\}$ NMR (δ): 11.5, 30.6, 96.2. Anal. calcd for $C_{22}H_{36}I_2Ru_2S_2$: C, 32.20; H, 4.42. Found: C, 32.06; H, 4.50. *anti*-**3a**: ^1H NMR (δ): 1.84 (s, 30H, Cp*), 3.14 (br, 6H, SMe). $^{13}C\{^1H\}$ NMR (δ): 11.6, 31.7, 96.3.

Preparation of 2b and 3b. To a suspension of $[\{Cp^*Ru(\mu_3\text{-}Br)\}_4]$ (495.1 mg, 0.391 mmol) in THF was added diisopropyl

(13) For an excellent review of halide effects in transition metal catalysis, see: (a) Fagnou, K.; Lautens, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 26, and references therein. For a recent example of halide effects in the ruthenium-catalyzed carbon-carbon bond forming reaction, see: (b) Nishimura, T.; Washitake, Y.; Uemura, S. *Adv. Synth. Catal.* **2007**, *349*, 2563.

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disulfide (1 mL, 6.3 mmol), and the mixture was stirred at reflux temperature for 24 h. After removal of the solvent, the residue was extracted with dichloromethane. Recrystallization from dichloromethane-*n*-hexane afforded dark-red thick plate crystals of **2b**·CH_2Cl_2 suitable for X-ray crystallographic study. The crystals were efflorescent and gave off dichloromethane by drying in vacuo to afford a dark-red powder of **2b** (325.3 mg, 0.416 mmol, 53%). ^{1}H NMR (δ): 1.44 (d, J = 7.0 Hz, 12H, CH*Me*$_2$), 1.65 (s, 30H, Cp*), 4.94 (sep, J = 7.0 Hz, 2H, C*H*Me$_2$). ^{13}C{^{1}H} NMR (δ): 11.0, 24.7, 40.5, 96.2. Anal. calcd for $C_{26}H_{44}Br_2Ru_2S_2$: C, 39.90; H, 5.67. Found: C, 39.96; H, 5.54.

3b was obtained as reddish-purple block crystals in 50% isolated yield in a similar reaction of [{Cp*Ru(μ_3-I)}$_4$] with diisopropyl disulfide. ^{1}H NMR (δ): 1.48 (d, J = 6.6 Hz, 12H, CH*Me*$_2$), 1.75 (s, 30H, Cp*), 5.27 (sep, J = 6.6 Hz, 2H, C*H*Me$_2$). ^{13}C{^{1}H} NMR (δ): 11.7, 26.2, 47.2, 96.4. Anal. calcd for $C_{26}H_{44}I_2Ru_2S_2$: C, 35.62; H, 5.06. Found: C, 35.43; H, 4.96.

Preparation of 2c$^+$Br$^-$ and 3c$^+$I$^-$. [{Cp*Ru(μ_3-Br)}$_4$] (62.2 mg, 0.049 mmol) and diphenyl disulfide (57.0 mg, 0.261 mmol) were dissolved in THF and the mixture was stirred at room temperature for 24 h. After removal of the solvent, the residue was extracted with dichloromethane. Recrystallization from dichloromethane-*n*-hexane afforded red plate crystals of **2c**$^+$Br$^-$·CH_2Cl_2 suitable for X-ray crystallographic study. The crystals were efflorescent and gave off dichloromethane by drying in vacuo to afford a red powder of **2c**$^+$Br$^-$ (21.5 mg, 0.025 mmol, 26%). ^{1}H NMR (δ): 1.55 (s, 30H, Cp*), 6.5−8.0 (m, 10H, Ph). Anal. calcd for $C_{32}H_{40}Br_2Ru_2S_2$: C, 45.18; H, 4.74. Found: C, 45.38; H, 4.55.

3c$^+$I$^-$ was obtained as brown block crystals in 37% isolated yield in a similar reaction of [{Cp*Ru(μ_3-I)}$_4$] with diphenyl disulfide. ^{1}H NMR (δ): 1.63 (s, 30H, Cp*), 6.5−6.9 (m, 2H, Ph), 7.4−7.8 (m, 6H, Ph), 7.9−8.2 (m, 2H, Ph). ^{13}C{^{1}H} NMR (δ): 11.0, 96.2, 129.5, 130.5, 131.9, 144.6. Anal. calcd for $C_{32}H_{40}I_2Ru_2S_2$: C, 40.68; H, 4.27. Found: C, 40.49; H, 4.31.

Ruthenium-Catalyzed Reaction of 1-Phenyl-2-propyn-1-ol with Nucleophiles.[1] A typical experimental procedure for the reaction of 1-phenyl-2-propyn-1-ol with aniline in the presence of **2b** (Table 1, run 8) is described below. To a mixture of **2b** (11.6 mg, 0.015 mmol) and NH_4BF_4 (3.2 mg, 0.031 mmol) dissolved in 1,2-dichloroethane (18 mL) were added 1-phenyl-2-propyn-1-ol (77.4 mg, 0.586 mmol) and aniline (279.4 mg, 3.000 mmol), and then the mixture was magnetically stirred at 60 °C for 1 h. The resulting mixture was dried up and the residue was purified by column chromatography (SiO_2, eluent *n*-hexane/ethyl acetate 90:10) to give *N*-(1-phenyl-2-propynyl)aniline (62.9 mg, 0.303 mmol, 52%).

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Supporting Information Available: Details of X-ray diffraction studies and a CIF file with crystallographic data for **1b**, **2b**·CH_2Cl_2, **3b**, **2c**$^+$Br$^-$·CH_2Cl_2, and **3c**$^+$I$^-$. This material is available free of charge via the Internet at http://pubs.acs.org.

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