Synthesis of Diruthenium Complexes Containing Chiral Thiolate-Bridged Ligands and Their Application to Catalytic Propargylic Alkylation of Propargylic Alcohols with Acetone

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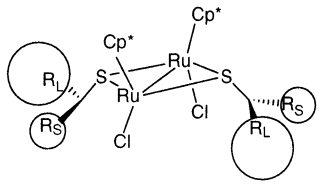
Summary: Novel diruthenium complexes containing chiral thiolate-bridged ligands are synthesized and characterized crystallographically. The chiral diruthenium complexes promote enantioselective propargylic alkylation of propargylic alcohols with acetone to give the corresponding propargylic alkylated products in good yields with moderate enantioselectivities (up to 35% ee).

Introduction

In sharp contrast to the transition metal-catalyzed highly enantioselective allylic substitution reaction of allylic alcohol derivatives with nucleophiles,[1,2] enantioselective propargylic substitution reaction of propargylic alcohol derivatives catalyzed by transition metal complexes has not yet been developed.[3,4] Quite recently, we have disclosed that the ruthenium-catalyzed propargylic substitution reaction of propargylic alcohols with various heteroatom- and carbon-centered nucleophiles gave the corresponding functionalized propargylic products in high yields with complete regioselectivities.[5−7] Noteworthy is that the reactions are catalyzed by thiolate-bridged diruthenium complexes such as [Cp*RuCl-(μ_2-SR)]$_2$ (Cp* = η^5-C_5Me_5; R = Me, Et, ^{n}Pr, ^{i}Pr).[8] The novel catalytic reaction proceeds via an allenylidene diruthenium complex as a key intermediate.[5−7,9] These findings prompted us to develop enantioselective propargylic substitution reactions in the presence of chiral ruthenium complexes. At first, we envisaged to design a new type of dinuclear ruthenium complexes with two chiral thiolate-bridged ligands, as shown in Chart 1, as the C_2-symmetric environment around the dinuclear complex should control an enantioselective attack of the nucleophile on the Cγ atom in the allenylidene moiety (vide infra). In contrast to transition metal catalysts with chiral phosphorus and nitrogen ligands, which have been reported to perform quite efficiently in a wide range of asymmetric reactions, the use of chiral sulfur ligands in asymmetric reactions catalyzed by transition metal complexes is still unexplored.[10] The preparation of diruthenium complexes containing chiral thiolate-bridged ligands and the catalytic propargylic alkylation using these complexes are reported here.

Chart 1. C_2-Symmetric Environment around the Dinuclear Ruthenium Complex with Chiral Thiolate-Bridged Ligands



Results and Discussion

When an equimolar mixture of the tetranuclear ruthenium(II) complex [Cp*Ru(μ_3-Cl)]$_4$ and (*R*,*R*)-bis-(1-phenylethyl) disulfide[11] was stirred in THF (tetrahydrofuran) at room temperature for 12 h, the chiral thiolate-bridged dinuclear ruthenium complex [Cp*RuCl-(μ_2-SR*)]$_2$ (**1a**; R* = (*R*)-PhCHMe) was obtained as a

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(8) The thiolate-bridged diruthenium complexes have been found to provide unique bimetallic reaction sites for activation and transformation of various terminal alkynes, see: Nishibayashi, Y.; Yamanashi, M.; Wakiji, I.; Hidai, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 2909, and references therein.

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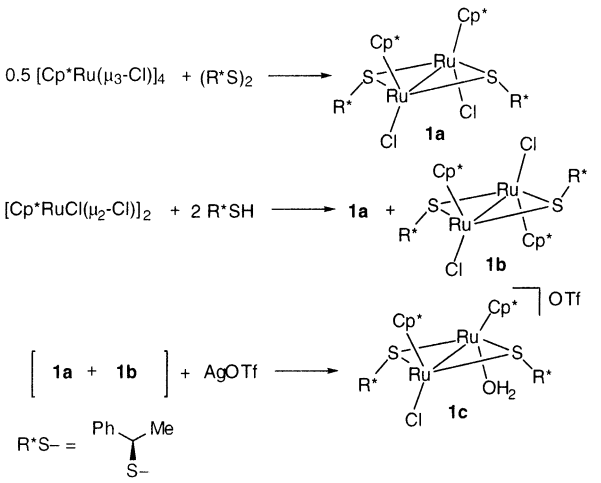
Scheme 1. Preparation of Dinuclear Ruthenium Complexes with Chiral Thiolate-Bridged Ligands



single isomer in 65% isolated yield (Scheme 1).[12] The molecular structure of **1a** was unambiguously established by X-ray analysis, and an ORTEP drawing is shown in Figure 1.[13] The dinuclear structure is doubly bridged by the μ_2-SR* moieties, and both the two Cp* and chloride ligands are present in *cis* configuration to each other. On the other hand, the reaction of the dinuclear ruthenium(III) complex [Cp*RuCl(μ_2-Cl)]$_2$ with (*R*)-1-phenylethanethiol[14] afforded a mixture of two chiral thiolate-bridged dinuclear ruthenium complexes (**1a** and **1b**) in 85% isolated yield. The ^{1}H and ^{13}C spectra of the mixture show the presence of two stereoisomers **1a** and **1b** in about 1:1 ratio. No isomerization was observed when the dinuclear ruthenium complexes were heated at 60 °C for 5 h. Further treatment of the mixture with an equimolar molar amount of AgOTf gave the corresponding cationic dinuclear ruthenium complex [Cp*RuCl(μ_2-SR*)$_2$RuCp*(OH$_2$)]OTf (**1c**) in 72% isolated yield as a single isomer (Scheme 1).[15] The molecular structure of **1c** was unambiguously determined by X-ray crystallography, and an ORTEP drawing is shown in Figure 2.[16] The ORTEP drawing displays an unsymmetrically substituted dinuclear structure, in which Cl and OH$_2$ ligands are coordinated to the respective ruthenium centers in mutual *cis* configuration. These results indicate that the reaction of both stereoisomers **1a** and **1b** with AgOTf gave one and the same stereoisomer **1c**.

Asymmetric propargylic alkylation of 1-phenyl-2-propyn-1-ol (**2a**) with acetone has been carried out in the presence of the chiral thiolate-bridged dinuclear ruthenium complexes. Typical results are shown in Table 1. Catalytic reaction even at 0 °C in the presence of **1a** (5 mol %) and NH_4BF_4 (10 mol %) proceeded smoothly to give 4-phenyl-5-hexyn-2-one (**3a**), but the enantioselectivity was low (Table 1, entry 3). When the cationic complex **1c** was used in place of **1a**, the enantioselectivity was slightly improved (Table 1, entry 4). In the presence of a mixture of **1a** and **1b**, the catalytic reaction proceeded similarly with the same selectivity (Table 1, entry 5), indicating that both stereoisomers **1a** and **1b** react with **2a** to give the same allenylidene diruthenium intermediate in the catalytic alkylation. Interestingly, the same result was obtained when the complex prepared in situ by treatment of [Cp*RuCl(μ_2-Cl)]$_2$ with (*R*)-1-phenylethanethiol at room temperature for 12 h was

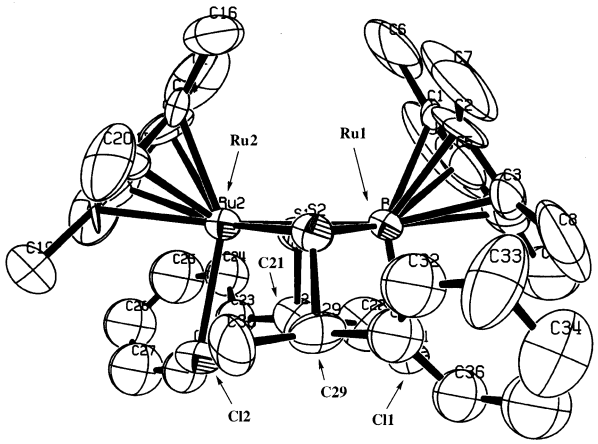


Figure 1. Crystal structure of **1a**. The hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ru(1)−Ru(2), 2.844(3); Ru(1)−S(1), 2.301(8); Ru(1)−S(2), 2.305(7); Ru(2)−S(1), 2.303(7); Ru(2)−S(2), 2.313(7); Ru(1)−Cl(1), 2.417(6); Ru(2)−Cl(1), 2.410(6); S(1)−C(21), 1.86(3); S(2)−C(29), 1.86(3); Ru(2)−Ru(1)−Cl(1), 99.6(2); Ru(1)−S(1)−Ru(2), 76.3(2); Ru(1)−S(2)−Ru(2), 76.0(2).

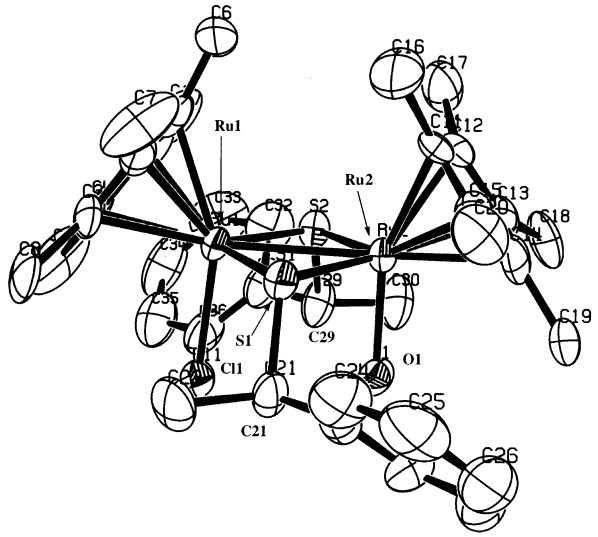


Figure 2. Crystal structure of **1c**. The hydrogen atoms and OTf anion are omitted for clarity. Selected distances (Å) and angles (deg): Ru(1)−Ru(2), 2.811(4); Ru(1)−S(1), 2.314(9); Ru(1)−S(2), 2.321(9); Ru(2)−S(1), 2.319(9); Ru(2)−S(2), 2.321(9); Ru(1)−Cl(1), 2.425(9); Ru(2)−O(1), 2.15(2); Ru(2)−Ru(1)−Cl(1), 95.8(2); Ru(1)−S(1)−Ru(2), 74.7(3); Ru(1)−S(2)−Ru(2), 74.5(3).

used as catalyst (Table 1, entry 6). Thus, the activity of the catalyst generated in situ from [Cp*RuCl(μ_2-Cl)]$_2$ and the corresponding thiol (R*SH) is almost the same

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(13) Crystal data for **1a**: $C_{36}H_{48}Cl_2Ru_2S_2$, M = 817.94, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 16.321(3) Å, b = 29.390(9) Å, c = 8.862(3) Å, V = 4251.0(2) Å^3, Z = 4, μ(Mo Kα) = 9.55 cm^{-1}, 5456 reflections measured, 1999 unique which were used in all calculations. Final R_1 = 0.057 and wR_2 = 0.068 (all data).
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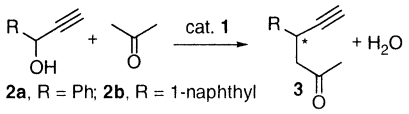
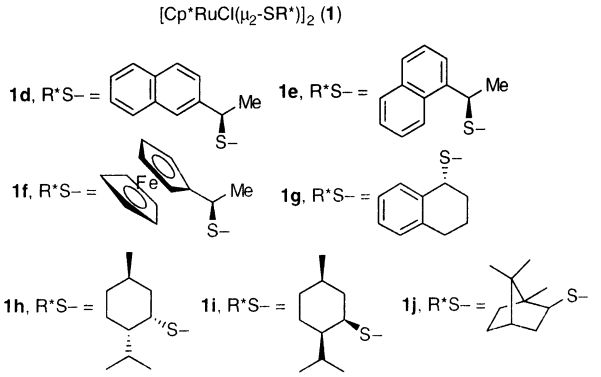
(16) Crystal data for **1c**: $C_{37}H_{50}ClF_3O_4Ru_2S_3$, M = 949.57, monoclinic, space group $P2_1$ (no. 4), a = 11.80(1) Å, b = 16.030(8) Å, c = 12.07(1) Å, β = 118.15(5)°, V = 2012.5(3) Å^3, Z = 2, μ(Mo Kα) = 10.23 cm^{-1}, 4941 reflections measured, 2726 unique which were used in all calculations. Final R_1 = 0.040 and wR_2 = 0.043 (all data).

Table 1. Ruthenium-Catalyzed Asymmetric Propargylic Alkylation of Propargylic Alcohols (2) with Acetone in the Presence of [Cp*RuCl(μ_2-SR*)]$_2$ (1)[a]



entry	alcohol	catalyst	reaction temp (°C)	reaction time (h)	yield of **3** (%)[b]	ee of **3** (%)[c]
1	**2a**	**1a**	60	3	95	11
2	**2a**	**1a**	25	20	95	10
3	**2a**	**1a**	0	140	95	10
4	**2a**	**1c**[d]	25	20	94	13
5	**2a**	**1a** + **1b**[e]	25	20	95	11
6	**2a**	**1a** + **1b**[f]	25	20	95	11
7	**2a**	**1d**[f]	60	3	77	15
8	**2a**	**1e**[f]	60	3	74	28
9	**2a**	**1f**[f]	60	3	0	
10	**2b**	**1e**[f]	60	3	41	35[g]

[a] All reactions were carried out in the presence of catalyst (**1**; 0.005 mmol) and NH_4BF_4 (0.01 mmol) using propargylic alcohol (**2**; 0.10 mmol) in acetone (5 mL). [b] GLC yield. [c] Determined by GLC. [d] In the absence of NH_4BF_4. [e] A mixture of **1a** and **1b** (1:1) was used. [f] Catalyst generated in situ from [Cp*RuCl(μ_2-Cl)]$_2$ and the corresponding thiol was used (see text). [g] Determined by HPLC.

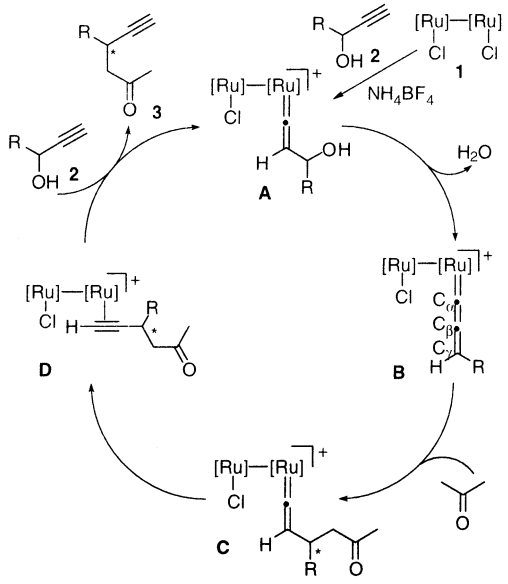


as that of the corresponding thiolate-bridged dinuclear ruthenium complex [Cp*RuCl(μ_2-SR*)]$_2$.

Next, the catalytic propargylic alkylation was carried out in the presence of catalysts generated in situ from [Cp*RuCl(μ_2-Cl)]$_2$ and other chiral thiols. When (*R*)-1-(2-naphthyl)ethanethiol and (*R*)-1-(1-naphthyl)ethanethiol were used as chiral ligands, higher enantioselectivities (15% and 28% ee, respectively) were obtained (Table 1, entries 7 and 8). In contrast, the use of (*R*)-1-ferrocenylethanethiol inhibited the catalytic alkylation (Table 1, entry 9). On the other hand, catalysts (**1g**−**j**) generated in situ with a variety of other chiral thiols promoted the propargylic alkylation of **2a** with acetone, but unfortunately **3a** was obtained with selectivity lower than 23% ee. When the reaction of 1-(1-naphthyl)-2-propyn-1-ol (**2b**) with acetone was carried out in the presence of **1e** generated in situ, the best enantioselectivity (35% ee) was obtained (Table 1, entry 10).

The plausible reaction pathway of the catalytic propargylic substitution reaction is shown in Scheme 2. Nucleophilic addition on the Cγ atom of the produced allenylidene complex[5−7] (**B**) gives a new vinylidene complex (**C**), which is transformed into an alkyne-ruthenium complex (**D**).[17] The reaction of the complex **D** with **2** results in the formation of the product **3** together with a starting vinylidene complex (**A**).[17] The enantioselectivity of this catalytic reaction is governed

Scheme 2



by the step of the nucleophilic attack of acetone on the complex **B** bearing chiral thiolate-bridged ligands.

In summary, we have prepared several diruthenium complexes containing chiral thiolate-bridged ligands and applied these complexes to catalytic and asymmetric propargylic alkylation of propargylic alcohols with acetone. Although the enantioselectivity is not yet satisfactory, the results described here provide the first example of enantioselective propargylic substitution reactions catalyzed by transition metal complexes. It is to be noted that the chiral thiolate-bridged ligands work to control the chiral environment around the diruthenium site. The result shows that chiral polymetallic clusters with sulfur ligands may offer new opportunities in asymmetric synthesis. Further work is currently in progress aimed at designing and preparing more effective chiral dinuclear ruthenium complexes.

Experimental Section

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a JEOL EX-400 spectrometer using $CDCl_3$ as solvent. Quantitative GLC analyses were performed on a Shimadzu GC-14B instrument equipped with a flame inonization detector using a 25 m × 0.25 mm CBP10 fused silica capillary column. GC−MS analyses were carried out on a Shimadzu GC-MS QP-5000 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHN analyzer or at Microanalytical Center of Kyoto University. Mass spectra were measured on a JEOL JMS600H mass spectrometer. All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by the usual methods and distilled before use. (*R*)-1-Phenylethanethiol,[14] (*R*,*R*)-bis(1-phenylethyl) disulfide,[11] (*R*)-1-ferrocenylethanethiol,[18] neomenthanethiol,[19] and (1*S*-*exo*)-2-bornanethiol[20] were prepared according to literature procedures.

Preparation of Chiral Thiols and Disulfides. A typical procedure for the preparation of (*R*)-1-(1-naphthyl)ethanethiol

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and (*R,R*)-bis(1-(1-naphthyl)ethyl) disulfide is as follows. To a solution of triphenylphosphine (7.65 g, 29.2 mmol) in THF (55 mL) at 0 °C was added diisopropyl azodicarboxylate (40% toluene solution, 16 mL, 29.0 mmol) dropwise. After stirring at 0 °C for 30 min, the mixture was treated dropwise with a solution of (*S*)-1-(1-naphthyl)ethanol (2.80 g, 16.3 mmol) and thiolacetic acid (2.21 g, 29.0 mmol) in THF (35 mL). After 1 h at 0 °C, the resulting solution was warmed to room temperature and stirred for 12 h. The reaction mixture was washed with saturated aqueous $NaHCO_3$ (25 mL × 4). The extract was concentrated under reduced pressure by an aspirator, and the residue was extracted with hexane (50 mL × 3). The hexane layer was concentrated and purified by column chromatography on SiO_2 with EtOAc/hexane (1:9) to give (*R*)-1-(1-naphthyl)ethyl thioacetate as a pale yellow oil (2.35 g, 10.1 mmol, 70.0% yield). To a solution of $LiAlH_4$ (435 mg, 11.5 mmol) in Et_2O (11 mL) at 0 °C was added dropwise a solution of the thioacetate (2.35 g, 10.1 mmol) in Et_2O (30 mL). The resulting mixture was stirred vigorously for 30 min at 0 °C, then warmed to room temperature, and stirred for an additional 30 min. The mixture was cooled to 0 °C and treated with 3 N aqueous HCl until all the solid had dissolved. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated to afford (*R*)-1-(1-naphthyl)ethanethiol as a pale yellow oil (1.73 g, 9.10 mmol, 63.0% yield): ^{1}H NMR δ 1.87 (d, 3H, J = 7.0 Hz), 2.13 (d, 1H, J = 5.4 Hz), 5.03 (dq, 1H, J = 7.0 and 5.4 Hz), 7.30−7.59 (m 3H), 7.66 (d, 1H, J = 6.8 Hz), 7.75 (d, 1H, J = 8.3 Hz), 7.87 (d, 1H, J = 7.9 Hz), 8.16 (d, 1H, J = 8.4 Hz).

A solution of iodine (40 mg, 0.16 mmol) in methanol (0.7 mL) was added dropwise to a solution of (*R*)-1-(1-naphthyl)-ethanethiol (49.1 mg, 0.260 mmol) in methanol (1.0 mL). After being stirred at room temperature for 2 days, sufficient 10% aqueous $Na_2S_2O_3$ was added to decolorize the solution. The organic layer was separated and washed with saturated $NaHCO_3$ and twice with water, dried ($MgSO_4$), and evaporated to give (*R,R*)-bis(1-(1-naphthyl)ethyl) disulfide as a white solid (48.7 mg, 0.13 mmol, 99.0% yield): ^{1}H NMR δ 1.69 (d, 6H, J = 6.8 Hz), 4.47 (q, 2H, J = 6.8 Hz), 7.28−7.63 (m, 10H), 7.75 (d, 2H, J = 8.3 Hz), 7.84 (d, 2H, J = 7.8 Hz); ^{13}C NMR δ 21.2, 45.2, 79.0, 123.2, 124.9, 125.3, 125.6, 126.0, 128.1, 128.9, 133.8, 138.1. Anal. Calcd for $C_{24}H_{22}S_2$: C, 76.96; H, 5.92. Found: C, 76.98; H, 6.12. The molecular structure was fully characterized by X-ray crystallography as shown in the Supporting Information (Figure S1).

(*R*)-1-(2-Naphthyl)ethanethiol and (*R,R*)-bis(1-(2-naphthyl)-ethyl) disulfide were prepared by the same method, and the physical, spectroscopic, and analytical data are as follows.

(*R*)-1-(2-Naphthyl)ethanethiol: white solid, 68% yield; ^{1}H NMR δ 1.76 (d, 3H, J = 6.8 Hz), 2.04 (d, 1H, J = 5.4 Hz), 4.40 (dq, 1H, J = 6.8 and 5.4 Hz), 7.37−7.83 (m 7H).

(*R,R*)-Bis(1-(2-naphthyl)ethyl) disulfide: white solid, 98% yield; ^{1}H NMR δ 1.62 (d, 6H, J = 7.1 Hz), 3.58 (q, 2H, J = 7.1 Hz), 7.38 (s, 2H), 7.45−7.51 (m, 4H), 7.70−7.82 (m, 8H); ^{13}C NMR δ 20.5, 50.0, 125.4, 125.9, 126.2, 126.7, 127.7, 127.9, 128.2, 132.8, 133.1, 139.5. Anal. Calcd for $C_{24}H_{22}S_2$: C, 76.96; H, 5.92. Found: C, 77.22; H, 6.09.

Preparation of [Cp*RuCl(μ_2-SR*)]$_2$ (1a; R* = (*R*)-PhCHMe) from [Cp*RuCl]$_4$ and Disulfide. To a suspension of [Cp*RuCl]$_4$ (58 mg, 0.054 mmol) in THF (1 mL) was added (*R,R*)-bis(1-phenylethyl) disulfide (29.0 mg, 0.106 mmol), and the mixture was stirred at room temperature for 12 h. A brown solid precipitated was filtered off, washed with *n*-hexane, and recrystallized from CH_2Cl_2/*n*-hexane to give brown crystals of **1a** (56 mg, 0.068 mmol, 65%): ^{1}H NMR δ 1.24 (s, 30H), 1.63 (d, 6H, J = 7.3 Hz), 6.18 (q, 2H, J = 7.3 Hz), 7.20−7.32 (m, 6H), 7.75−7.80 (m, 4H). Anal. Calcd for $C_{36}H_{48}Cl_2Ru_2S_2$: C 52.86, H 5.91. Found: C 52.75, H 5.78.

Preparation of [Cp*RuCl(μ_2-SR*)]$_2$ (1a and 1b; R* = (*R*)-PhCHMe) from [Cp*RuCl$_2$]$_2$ and Thiol. To a suspension of [Cp*RuCl$_2$]$_2$ (614 mg, 1.00 mmol) in THF (30 mL) was added (*R*)-1-phenylethanethiol (276 mg, 2.00 mmol), and the mixture was stirred at room temperature for 12 h. After evaporation of the solvent under vacuum, the residue was extracted with CH_2Cl_2. Addition of *n*-hexane to the CH_2Cl_2 solution afforded brown crystals (695 mg, 0.850 mmol, 85.0%) as a mixture of two chiral thiolate-bridged dinuclear ruthenium complexes (**1a** and **1b**): ^{1}H NMR δ 1.24 (s, 30H), 1.31 (s, 30H), 1.63 (d, 6H, J = 7.3 Hz), 1.74 (d, 6H, J = 7.3 Hz), 5.82 (q, 2H, J = 7.3 Hz), 6.18 (q, 2H, J = 7.3 Hz), 7.20−7.32 (m, 12H), 7.75−7.80 (m, 8H).

Preparation of [Cp*RuCl(μ_2-SR*)$_2$RuCp*(OH$_2$)]OTf (1c; R* = (*R*)-PhCHMe). In a 50 mL flask was placed a mixture of **1a** and **1b** (96.0 mg, 0.117 mmol) under N_2. Anhydrous THF (3 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of AgOTf (27.0 mg, 0.105 mmol), the reaction flask was kept at room temperature for 12 h. Then, the solvent was removed under reduced pressure, and the residue was recrystallized from CH_2Cl_2/*n*-hexane to give black crystals of **1c** (71.8 mg, 0.076 mmol, 72%): ^{1}H NMR δ 1.32 (s, 30H), 1.79 (d, 6H, J = 7.0 Hz), 5.20 (br, 2H), 7.24−7.65 (m, 20H). Anal. Calcd for $C_{37}H_{50}ClF_3O_4Ru_2S_3$: C, 46.80; H, 5.31. Found: C, 46.62; H, 5.08.

Ruthenium-Catalyzed Asymmetric Propargylic Alkylation of Propargylic Alcohols with Ketones. A typical experimental procedure for the reaction of 1-phenyl-2-propyn-1-ol (**2a**) with acetone catalyzed by **1a** is described below. In a 50 mL flask were placed **1a** (0.005 mmol) and NH_4BF_4 (0.010 mmol) under N_2. Anhydrous acetone (5 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **2a** (0.10 mmol), the reaction flask was kept at 60 °C for 3 h. The reaction mixture was treated with brine (150 mL) and extracted with diethyl ether (20 mL × 3). The ether layer was dried over anhydrous $MgSO_4$. For isolation, the extract was concentrated under reduced pressure by an aspirator, and then the residue was purified by TLC (SiO_2) with EtOAc/hexane (1:9) to give 4-phenyl-5-hexyn-2-one (**3a**) as a yellow solid (14.6 mg, 0.085 mmol, 85.0% yield): ^{1}H NMR δ 2.13 (s, 3H), 2.26 (s, 1H), 2.80 (dd, 1H, J = 16 and 5.2 Hz), 3.00 (dd, 1H, J = 16 and 8.4 Hz), 4.20 (br, 1H), 7.22−7.39 (m, 5H); ^{13}C NMR δ 30.4, 32.4, 51.5, 71.0, 84.8, 127.1, 127.2, 128.6, 140.1, 205.4; IR (KBr, cm^{-1}) 1720 (*C*═*O*), 2118 (*C*≡*C*), 3291 (≡*C*−*H*). Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.41; H, 7.00. The ee value of **3a** was determined by GLC on a cyclodextrin phase (Chiraldex GT-A, 30 m).

4-(1-Naphthyl)-5-hexyn-2-one (3b): pale yellow oil; ^{1}H NMR δ 2.20 (s, 3H), 2.33 (s, 1H), 2.92 (dd, 1H, J = 17 and 3.9 Hz), 3.11 (dd, 1H, J = 17 and 10.0 Hz), 4.99 (d, 1H, J = 9.3 Hz), 7.42−7.56 (m, 3H), 7.76 (t, 2H, J = 7.8 Hz), 7.87 (d, 1H, J = 7.8 Hz), 8.05 (d, 1H, J = 8.3 Hz); ^{13}C NMR δ 29.1, 30.6, 50.5, 71.6, 84.8, 122.6, 125.1, 125.5, 125.7, 126.4, 128.0, 129.1, 130.1, 134.0, 135.6, 205.7; IR (neat, cm^{-1}) 2116 (*C*≡*C*), 3291 (≡*C*−*H*). Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.11; H, 6.26. The ee value of **3b** was determined by HPLC on a Daicel Chiralcel OD column (hexane/^{i}PrOH, 90:10).

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Supporting Information Available: Experimental procedures and crystallographic data for (*R,R*)-bis(1-(1-naphthyl)-ethyl) disulfide, **1a**, and **1c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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