

# Preparation of a Series of Chalcogenolate-Bridged Diruthenium Complexes and Their Catalytic Activities toward Propargylic Substitution Reactions

Yoshiaki Nishibayashi,<sup>\*,†</sup> Hiroaki Imajima,<sup>†</sup> Gen Onodera,<sup>†</sup>  
Masanobu Hidai,<sup>‡</sup> and Sakae Uemura<sup>\*,†</sup>

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering,  
Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan, and Department of  
Materials Science and Technology, Faculty of Industrial Science and Technology,  
Tokyo University of Science, Noda, Chiba 278-8510, Japan

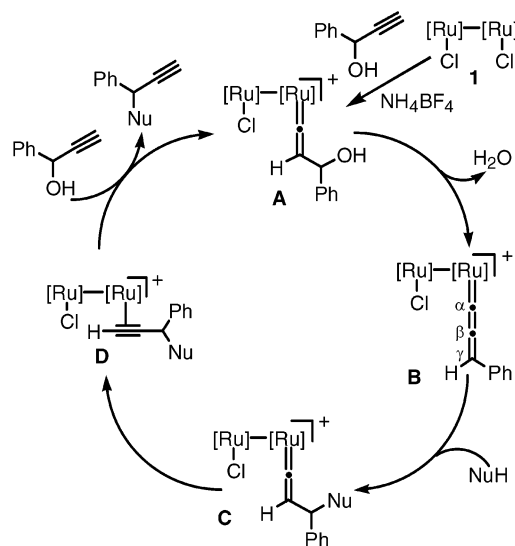
Received August 28, 2003

A series of chalcogenolate(Se,Te)-bridged diruthenium complexes (neutral and cationic) as well as their allenylidene complexes have been newly prepared, and their catalytic activities toward the propargylic substitution reactions have been compared with those using the corresponding thiolate(S)-bridged complexes. Results of both catalytic and stoichiometric reactions using these complexes together with their redox properties show that the ease of the charge transfer from one Ru atom (working as an electron pool) to the other in the complexes (synergistic effect) may be one of the important factors in promoting a key ligand exchange step for these catalytic reactions. The finding presented here may provide a new possibility of polynuclear transition metal complexes for organic transformations.

## Introduction

We have recently disclosed the ruthenium-catalyzed efficient propargylic substitution reactions of propargylic alcohols with various heteroatom- and carbon-centered nucleophiles to afford the corresponding propargylated products in high yields with a complete regioselectivity.<sup>1</sup> The reactions are catalyzed by thiolate-bridged diruthenium complexes such as  $[\text{Cp}^*\text{RuCl}(\mu_2\text{-SR})_2]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ;  $\text{R} = \text{Me}$  (**1a**),  $n\text{Pr}$ ,  $i\text{Pr}$ ) and  $[\text{Cp}^*\text{RuCl}(\mu_2\text{-SMe})_2\text{-RuCp}^*(\text{OH}_2)]\text{OTf}$  ( $\text{OTf} = \text{OSO}_2\text{CF}_3$ ) (**1b**) but not by various monoruthenium complexes<sup>2</sup> which have been known to work as reagents for stoichiometric propargylic substitution reactions.<sup>3</sup> Results of some stoichiometric and catalytic reactions indicate that the propargylic substitution reactions proceed via allenylidene intermediates as shown in Scheme 1, where only one of the two Ru atoms works as a reactive site throughout the reaction.<sup>4–6</sup> Here, the reason only the diruthenium

Scheme 1



complexes are effective for these catalytic reactions seems to be that one Ru moiety, which is not involved in allenylidene formation, works as an electron pool or a mobile ligand to another Ru site (Scheme 2), by taking into account the theoretical report of synergistic effects

\* To whom correspondence should be addressed. E-mail: ynishiba@scl.kyoto-u.ac.jp (Y.N.); uemura@scl.kyoto-u.ac.jp (S.U.).

<sup>†</sup> Kyoto University.

<sup>‡</sup> Tokyo University of Science.

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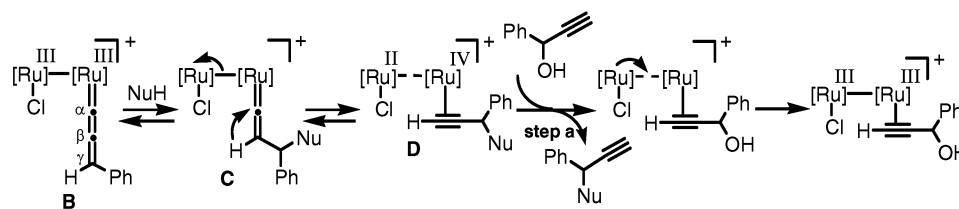
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Scheme 2



Scheme 3

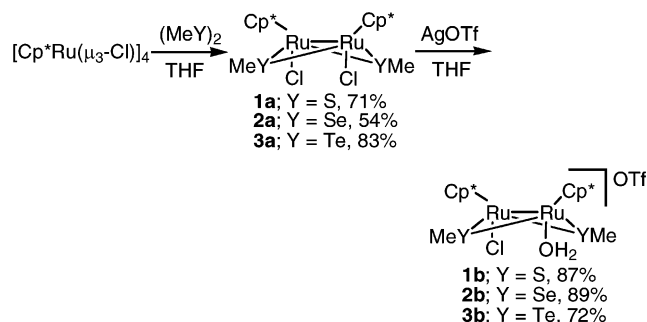
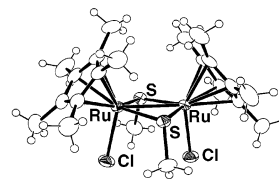
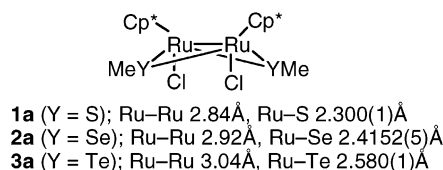


Chart 1



of two equal Rh metals in the dirhodium-catalyzed reaction between a diazo compound and an alkane.<sup>7</sup>

To obtain some experimental evidence for this synergistic effect in our case, we have prepared a series of chalcogenolate(Se,Te)-bridged diruthenium complexes and compared their catalytic activities with those of previously prepared thiolate(S)-bridged complexes in propargylic substitution reactions. We describe here the results and discuss the relation between Ru–Ru bond lengths in the complexes as well as their redox potentials and catalytic activities, to clarify the role of the two Ru moieties.

## Results and Discussion

When an equimolar mixture of the tetranuclear ruthenium(II) complex  $[\text{Cp}^*\text{Ru}(\mu_3\text{-Cl})]_4$  and dimethyl diselenide was stirred in tetrahydrofuran (THF) at room temperature for 20 h, the methaneselenolate-bridged diruthenium complex  $[\text{Cp}^*\text{RuCl}(\mu_2\text{-SeMe})]_2$  (**2a**) was obtained in 54% isolated yield after recrystallization (Scheme 3). Treatment of **2a** with an equimolar amount of AgOTf gave the corresponding cationic diruthenium complex  $[\text{Cp}^*\text{RuCl}(\mu_2\text{-SeMe})_2\text{RuCp}^*(\text{OH}_2)]\text{OTf}$  (**2b**) in 89% isolated yield as a single isomer. Similarly, the methanetellurolate-bridged diruthenium complexes  $[\text{Cp}^*\text{RuCl}(\mu_2\text{-TeMe})]_2$  (**3a**) and  $[\text{Cp}^*\text{RuCl}(\mu_2\text{-TeMe})_2\text{RuCp}^*(\text{OH}_2)]\text{OTf}$  (**3b**) were prepared using dimethyl ditelluride in 83% and 72% isolated yields, respectively.

The molecular structures of all these complexes, including the already prepared S analogues (Scheme 3), were unambiguously determined by X-ray analysis, and their ORTEP drawings are shown in the Supporting Information. The Ru–Ru bond distance (3.04 Å) of **3a** is longer than those observed for the thiolate- and selenolate-bridged complexes (**1a**, 2.84 Å; **2a**, 2.92 Å), and it is slightly longer than a typical Ru–Ru single bond (2.71–3.02 Å).<sup>8</sup> Selected bond lengths of **1a**, **2a**,

and **3a** are summarized in Chart 1. Although the diamagnetic nature of **3a** suggests the existence of a bonding interaction between the two Ru(III) atoms, we cannot exclude the possibility that the diamagnetism of complex **3a** might be due to some exchange interaction via the orbitals of the bridging Te by considering a longer Ru–Ru bond.

Next, catalytic activities of **1–3** toward the propargylic substitution reactions were investigated for comparison. Treatment of 1-phenyl-2-propyn-1-ol (**4a**) with acetone in the presence of **1a** or **2a** (5 mol %) and  $\text{NH}_4\text{BF}_4$  (10 mol %) at reflux temperature for 3 h afforded 4-phenyl-5-hexyn-2-one (**5a**) in 88% or 95% isolated yield, respectively (Table 1, runs 1 and 2). Surprisingly, no propargylic alkylation occurred in the presence of **3a** under the same reaction conditions (Table 1, run 3). When the reaction of **4a** with acetone was carried out in the presence of a cationic complex such as **1b** or **2b** (2.5 mol %), **5a** was obtained in 93% or 95% GLC yield, respectively (Table 2, runs 1 and 2). In sharp contrast, again no catalytic reaction proceeded at all in the presence of **3b** (Table 2, run 3).

A similar phenomenon, a difference of catalytic activity, was also observed in propargylic substitution reactions of **4a** with various other nucleophiles such as alcohol, amine, amide, and aromatic compounds. Typical results are shown in Tables 1 and 2. Thus, the catalytic use of **1** or **2** resulted in the formation of the corresponding propargylated products in moderate to high yields with complete regioselectivity, while the corresponding propargylated products were not obtained by use of **3**.

Reactions of cationic selenolate- and tellurolate-bridged diruthenium complexes **2b** and **3b** with 1 equiv of 1,1-bis(4'-methylphenyl)-2-propyn-1-ol (**4b**) in 1,2-dichloroethane at room temperature for 1 h afforded the allenylidene complexes **2c** and **3c** in 94% and 91% isolated yields, respectively, as in the case of the corresponding thiolate complex **1c**<sup>1a</sup> (Scheme 4). The structures of allenylidene complexes are supported by

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**Table 1. Propargylic Substitution Reactions of Propargylic Alcohol (4a) with Nucleophiles Using a Neutral Ru Complex as Catalyst<sup>a</sup>**

$\text{Ph}-\text{CH}(\text{OH})-\text{C}\equiv\text{CH} \text{ (4a)} + \text{NuH} \xrightarrow{5 \text{ mol\% catalyst}} \text{Ph}-\text{CH}(\text{Nu})-\text{C}\equiv\text{CH} \text{ (5)} + \text{H}_2\text{O}$					
run	nucleophile	catalyst	reaction temp. (°C)	reaction time (h)	yield (%) <sup>b</sup>
1		1a	reflux <sup>c</sup>	3	88
2		2a	reflux <sup>c</sup>	3	95
3		3a	reflux <sup>c</sup>	3	0
4	EtOH	1a	60 <sup>d</sup>	1	81
5		2a	60 <sup>d</sup>	1	80
6		3a	60 <sup>d</sup>	1	2
7	PhNH <sub>2</sub> <sup>e</sup>	1a	60 <sup>f</sup>	1	80
8		2a	60 <sup>f</sup>	1	95
9		3a	60 <sup>f</sup>	1	0
10		1a	60 <sup>f</sup>	3	74
11		2a	60 <sup>f</sup>	3	80
12		3a	60 <sup>f</sup>	3	0
13		1a	60 <sup>f</sup>	1	94
14		2a	60 <sup>f</sup>	1	81
15		3a	60 <sup>f</sup>	1	2

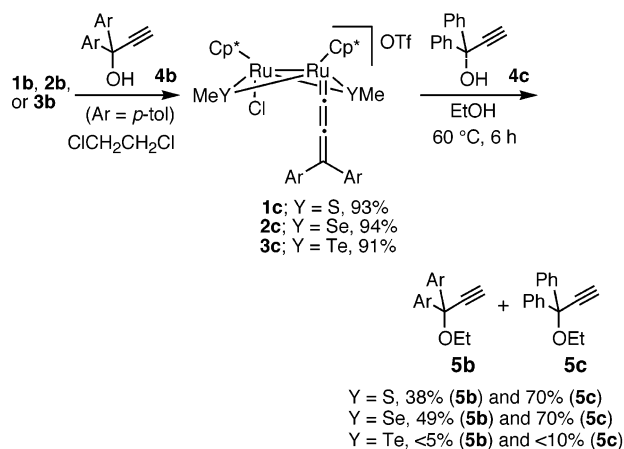
<sup>a</sup> All the reactions of **4a** (0.60 mmol) with nucleophile were carried out in the presence of catalyst (5 mol %) and NH<sub>4</sub>BF<sub>4</sub> (10 mol %). <sup>b</sup> Isolated yield. <sup>c</sup> Acetone was used as solvent. <sup>d</sup> Ethanol was used as solvent. <sup>e</sup> Aniline (5 equiv) was used as nucleophile. <sup>f</sup> ClCH<sub>2</sub>CH<sub>2</sub>Cl was used as solvent. <sup>g</sup> 2-Pyrrolidinone (5 equiv) was used as nucleophile. <sup>h</sup> 2-Methylfuran (10 equiv) was used as nucleophile.

**Table 2. Propargylic Substitution Reactions of Propargylic Alcohol (4a) with Nucleophiles Using a Cationic Ru Complex as Catalyst<sup>a</sup>**

$\text{Ph}-\text{CH}(\text{OH})-\text{C}\equiv\text{CH} \text{ (4a)} + \text{NuH} \xrightarrow{5 \text{ mol\% catalyst}} \text{Ph}-\text{CH}(\text{Nu})-\text{C}\equiv\text{CH} \text{ (5)} + \text{H}_2\text{O}$					
run	nucleophile	catalyst	reaction temp. (°C)	reaction time (h)	yield (%) <sup>b</sup>
1		1b <sup>c</sup>	reflux <sup>d</sup>	3	93 <sup>e</sup>
2		2b <sup>c</sup>	reflux <sup>d</sup>	3	95 <sup>e</sup>
3		3b <sup>c</sup>	reflux <sup>d</sup>	3	0 <sup>e</sup>
4	EtOH	1b	60 <sup>f</sup>	1	96 <sup>e</sup>
5		2b	60 <sup>f</sup>	1	94 <sup>e</sup>
6		3b	60 <sup>f</sup>	1	4
7	PhNH <sub>2</sub> <sup>g</sup>	1b	60 <sup>h</sup>	1	>95
8		2b	60 <sup>h</sup>	1	>95
9		3b	60 <sup>h</sup>	1	0
10		1b	60 <sup>h</sup>	3	86
11		2b	60 <sup>h</sup>	3	88
12		3b	60 <sup>h</sup>	3	0
13		1b	60 <sup>h</sup>	1	89
14		2b	60 <sup>h</sup>	1	84
15		3b	60 <sup>h</sup>	1	0

<sup>a</sup> All the reactions of **4a** (0.60 mmol) with nucleophile were carried out in the presence of catalyst (5 mol %). <sup>b</sup> Isolated yield. <sup>c</sup> Catalyst (2.5 mol %) was used. <sup>d</sup> Acetone was used as solvent. <sup>e</sup> GLC yield. <sup>f</sup> Ethanol was used as solvent. <sup>g</sup> Aniline (5 equiv) was used as nucleophile. <sup>h</sup> ClCH<sub>2</sub>CH<sub>2</sub>Cl was used as solvent. <sup>i</sup> 2-Pyrrolidinone (5 equiv) was used as nucleophile. <sup>j</sup> 2-Methylfuran (10 equiv) was used as nucleophile.

the spectral data of **2c** and **3c** by comparison with the previous data of **1c**. The molecular structure of **1c** has

**Scheme 4**

previously been clarified by an X-ray study.<sup>1a</sup> Treatment of **1c** or **2c** with 3 equiv of 1,1-diphenyl-2-propyn-1-ol (**4c**) in EtOH at 60 °C for 6 h gave **5b** in 38% or 49% yield together with **5c** in 70% yield, respectively. However, in the reaction of **3c** with **4c**, only a quite low yield of **5b** as well as **5c** was obtained. This fact clearly shows that, in the tellurolate case, either the step of a nucleophilic attack on C<sub>γ</sub> (**B** → **C** in Scheme 1) in the allenylidene moiety of **3c** does not proceed smoothly or the ligand exchange with another propargylic alcohol (**D** → **A** in Scheme 1) does not occur readily.

To obtain more information on the reaction mechanism, the redox properties of **1b**, **2b**, and **3b** were examined by cyclic voltammetry.<sup>9</sup> The cyclic voltammograms of **1b** and **2b** revealed two reversible waves at  $E_{1/2} = +0.58$ , +1.15 V and  $E_{1/2} = +0.53$ , +1.11 V, respectively, assignable to the redox couples [Ru<sup>III</sup>/Ru<sup>IV</sup>] and [Ru<sup>IV</sup>/Ru<sup>IV</sup>]. In contrast, the cyclic voltammogram of **3b** exhibited one irreversible wave at  $E_p = +1.91$  V. This finding shows that the oxidation (namely, an electron transfer) of **1b** and **2b** proceeds more smoothly than that of **3b**. The charge transfer from one Ru atom to the other in the S and Se cases facilitates the ligand exchange between alkynes on **D** and propargylic alcohol (**step a** in Scheme 2) because of the higher oxidation state of Ru<sup>IV</sup> reducing the back-donation ability from the Ru to the coordinated alkyne moiety of **D**. The difficulty of the charge transfer in the tellurolate case corresponds to a quite low catalytic activity of **3a** and **3b**.

## Conclusion

A series of chalcogenolate(Se,Te)-bridged diruthenium complexes (neutral and cationic) as well as their allenylidene complexes were newly prepared, and their catalytic activities toward the propargylic substitution reactions were compared with those of the correspond-

(9) In CH<sub>2</sub>Cl<sub>2</sub>/[<sup>n</sup>Bu<sub>4</sub>N]BF<sub>4</sub> (0.002 mmol/ml), with a scan rate of 0.1 V s<sup>-1</sup> and a saturated calomel electrode (SCE) reference electrode.

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ing thiolate-bridged ones already prepared. As a result, it was revealed that S- and Se-bridged complexes were quite effective as catalysts for many propargylic substitution reactions, while Te-bridged complexes did not show any catalytic activity. By comparison of these results with the structure of these complexes determined by X-ray studies as well as their redox potentials, it can be proposed that the charge transfer from one Ru atom to the other may be one of the important factors for the above catalytic reactions, one Ru moiety working as an electron pool or a mobile ligand to another Ru moiety (synergistic effect).

## Experimental Section

**General Method.**  $^1\text{H}$  NMR (400, 300, and 270 MHz) and  $^{13}\text{C}$  NMR (100, 75, and 67.8 MHz) spectra were recorded using  $\text{CDCl}_3$  as solvent. Quantitative GLC analyses were performed on a Shimadzu GC-14A instrument equipped with a flame ionization detector using a  $25\text{ m} \times 0.25\text{ mm}$  CBP10 fused silica capillary column. GC-MS analyses were carried out on a Shimadzu GC-MS QP-5000 spectrometer. Elemental analyses were performed at the 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.

**Preparation of the Methanechalcogenolate-Bridged Diruthenium Complex  $[\text{Cp}^*\text{RuCl}(\mu_2\text{-YMe})_2]_2$  ( $\text{Y} = \text{S}, \text{Se}, \text{Te}$ ).** A typical experimental procedure for the preparation of  $[\text{Cp}^*\text{RuCl}(\mu_2\text{-SMe})_2]_2$  (**1a**) is described below. To a suspension of  $[\text{Cp}^*\text{RuCl}]_4$  (498 mg, 0.46 mmol) in THF (20 mL) was added dimethyl disulfide (86.7 mg, 0.92 mmol), and the mixture was stirred at room temperature for 24 h. The solvent was then removed under vacuum. The residue was recrystallized from  $\text{CH}_2\text{Cl}_2$ -*n*-hexane to give black crystals of **1a** (410 mg, 0.64 mmol, 71%).  $^1\text{H}$  NMR:  $\delta$  1.62 (s, 30H,  $\text{C}_5\text{Me}_5$ ), 2.51 (s, 6H, *SMe*). Anal. Calcd for  $\text{C}_{22}\text{H}_{36}\text{Cl}_2\text{Ru}_2\text{S}_2$ : C, 41.44; H, 5.69. Found: C, 41.32; H, 5.69. The same complex has also been prepared by treatment of  $[\text{Cp}^*\text{RuCl}]_2$  with  $\text{MeSSiMe}_3$ .<sup>1a</sup>

Spectroscopic data and isolated yields of other complexes are as follows.

**$[\text{Cp}^*\text{RuCl}(\mu_2\text{-SeMe})_2]_2$  (**2a**):** yield 54%; black crystals.  $^1\text{H}$  NMR:  $\delta$  1.63 (s, 30H,  $\text{C}_5\text{Me}_5$ ), 2.44 (s, 6H, *SeMe*). Anal. Calcd for  $\text{C}_{22}\text{H}_{36}\text{Cl}_2\text{Ru}_2\text{Se}_2$ : C, 36.12; H, 4.96. Found: C, 35.93; H, 4.75.

**$[\text{Cp}^*\text{RuCl}(\mu_2\text{-TeMe})_2]_2$  (**3a**):** yield 83%; black crystals.  $^1\text{H}$  NMR:  $\delta$  1.70 (s, 30H,  $\text{C}_5\text{Me}_5$ ), 2.20 (s, 6H, *TeMe*). Anal. Calcd for  $\text{C}_{22}\text{H}_{36}\text{Cl}_2\text{Ru}_2\text{Te}_2$ : C, 31.88; H, 4.38. Found: C, 31.74; H, 4.34.

**Preparation of Cationic Methanechalcogenolate-Bridged Diruthenium Complexes  $[\text{Cp}^*\text{RuCl}(\mu_2\text{-YMe})_2\text{RuCp}^*(\text{OH}_2)]\text{OTf}$  ( $\text{Y} = \text{S}, \text{Se}, \text{Te}$ ).** A typical experimental procedure for the preparation of  $[\text{Cp}^*\text{RuCl}(\mu_2\text{-SMe})_2\text{RuCp}^*(\text{OH}_2)]\text{OTf}$  (**1b**)<sup>1d</sup> is described below. In a 50 mL flask was placed **1a** (965 mg, 1.51 mmol) under  $\text{N}_2$ . Anhydrous tetrahydrofuran (THF) (20 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of  $\text{AgOTf}$  (398 mg, 1.55 mmol), the reaction flask was kept at room temperature for 20 h. Then, the solvent was removed under reduced pressure, and the residue was recrystallized from  $\text{CH}_2\text{Cl}_2$ -*n*-hexane to give black crystals of  $[\text{Cp}^*\text{RuCl}(\mu_2\text{-SMe})_2\text{RuCp}^*(\text{OH}_2)]\text{OTf}$  (**1b**; 1.02 g, 1.32 mmol, 87%).  $^1\text{H}$  NMR:  $\delta$  1.63 (s, 30H,  $\text{C}_5\text{Me}_5$ ), 2.51 (s, 6H, *SMe*), 3.30 (brs, 2H,  $\text{OH}_2$ ).  $^{13}\text{C}$  NMR:  $\delta$  1.1, 10.5, 96.5. Anal. Calcd for  $\text{C}_{23}\text{H}_{38}\text{ClF}_3\text{O}_4\text{Ru}_2\text{S}_3$ : C, 35.91; H, 4.98. Found: C, 35.78; H, 4.11.

Spectroscopic data and isolated yields of other complexes are as follows.

**$[\text{Cp}^*\text{RuCl}(\mu_2\text{-SeMe})_2\text{RuCp}^*(\text{OH}_2)]\text{OTf} \cdot \text{CH}_2\text{Cl}_2$  (**2b**· $\text{CH}_2\text{Cl}_2$ ):** yield 89%; black crystals.  $^1\text{H}$  NMR:  $\delta$  1.69 (s, 30H,

$\text{C}_5\text{Me}_5$ ), 2.49 (s, 6H, *SeMe*). Anal. Calcd for  $\text{C}_{23}\text{H}_{38}\text{ClF}_3\text{O}_4\text{Ru}_2\text{Se}_2 \cdot \text{CH}_2\text{Cl}_2$ : C, 30.41; H, 4.25. Found: C, 30.67; H, 4.14.

**$[\text{Cp}^*\text{RuCl}(\mu_2\text{-TeMe})_2\text{RuCp}^*(\text{OH}_2)]\text{OTf}$  (**3b**):** yield 72%; black crystals.  $^1\text{H}$  NMR:  $\delta$  1.83 (s, 30H,  $\text{C}_5\text{Me}_5$ ), 2.52 (s, 6H, *TeMe*). Anal. Calcd for  $\text{C}_{23}\text{H}_{38}\text{ClF}_3\text{O}_4\text{Ru}_2\text{STe}_2$ : C, 28.76; H, 3.99. Found: C, 28.57; H, 3.84.

**Ruthenium-Catalyzed Propargylic Substitution Reactions of Propargylic Alcohols with Nucleophiles.** A typical experimental procedure for the reaction of 1-phenyl-2-propyn-1-ol (**4a**) with acetone catalyzed by  $[\text{Cp}^*\text{RuCl}(\mu_2\text{-SMe})_2]_2$  (**1a**) is described below. In a 50 mL flask were placed **1a** (0.03 mmol) and  $\text{NH}_4\text{BF}_4$  (0.06 mmol) under  $\text{N}_2$ . Anhydrous acetone (36 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **4a** (0.60 mmol), the reaction flask was kept at reflux temperature for 4 h. The reaction mixture was treated with brine (150 mL) and extracted with diethyl ether (20 mL  $\times$  3). The ether layer was dried over anhydrous  $\text{MgSO}_4$ . For isolation, the extract was concentrated under reduced pressure by an aspirator, and then the residue was purified by TLC ( $\text{SiO}_2$ ) with  $\text{EtOAc}$ -hexane (1/9) as an eluent to give **5a** as a yellow solid (91 mg, 0.53 mmol, 88% yield).

**4-Phenyl-5-hexyn-2-one (**5a**):**<sup>1b</sup>  $^1\text{H}$  NMR:  $\delta$  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).  $^{13}\text{C}$  NMR:  $\delta$  30.4, 32.4, 51.5, 71.0, 84.8, 127.1, 127.2, 128.6, 140.1, 205.4. IR (KBr,  $\text{cm}^{-1}$ ): 1720 (C=O), 2118 (C $\equiv$ C), 3291 ( $\equiv$ CH). Anal. Calcd for  $\text{C}_{12}\text{H}_{12}\text{O}$ : C, 83.69; H, 7.02. Found: C, 83.41; H, 7.00.

Spectroscopic data of other products are as follows.

**(1-Ethoxy-2-propynyl)benzene:**<sup>1a</sup> pale yellow oil.  $^1\text{H}$  NMR:  $\delta$  1.26 (t, 3H,  $J = 7.0$  Hz), 2.63 (d, 1H,  $J = 2.0$  Hz), 3.55 (qd, 1H,  $J = 7.0$  and 8.8 Hz), 3.75 (qd, 1H,  $J = 7.0$  and 8.8 Hz), 5.16 (d, 1H,  $J = 2.0$  Hz), 7.33–7.40 (m, 3H), 7.52 (d, 2H,  $J = 7.3$  Hz).  $^{13}\text{C}$  NMR:  $\delta$  15.1, 63.9, 71.1, 75.3, 81.8, 127.3, 128.4, 128.5, 138.3. IR (neat,  $\text{cm}^{-1}$ ): 2114 (C $\equiv$ C), 3293 ( $\equiv$ CH). Anal. Calcd for  $\text{C}_{11}\text{H}_{12}\text{O}$ : C, 82.46; H, 7.55. Found: C, 82.56; H, 7.47.

**Phenyl(1-phenyl-2-propynyl)amine:** pale yellow oil.  $^1\text{H}$  NMR:  $\delta$  2.43 (d, 1H,  $J = 2$  Hz), 4.01 (br, 1H), 5.26 (s, 1H), 6.69 (d, 2H,  $J = 8$  Hz), 6.77 (d, 1H,  $J = 7$  Hz), 7.16–7.21 (m, 2H), 7.30–7.38 (m, 3H), 7.58 (d, 2H,  $J = 7$  Hz).  $^{13}\text{C}$  NMR:  $\delta$  49.7, 73.1, 82.9, 113.9, 118.7, 127.1, 128.1, 128.7, 129.1, 138.9, 146.2. IR (KBr,  $\text{cm}^{-1}$ ): 2114 (C $\equiv$ C), 3279 ( $\equiv$ CH), 3372 (NH). Anal. Calcd for  $\text{C}_{15}\text{H}_{13}\text{N}$ : C, 86.92; H, 6.32; N, 6.76. Found: C, 86.70; H, 6.68; N, 7.10.

**1-(1-Phenyl-2-propynyl)-2-pyrrolidinone:** yellow oil.  $^1\text{H}$  NMR:  $\delta$  1.86–2.03 (m, 2H), 2.40–2.46 (m, 2H), 2.55 (d, 1H,  $J = 2.2$  Hz), 2.97–3.03 (m, 1H), 3.49–3.55 (m, 1H), 6.31 (d, 1H,  $J = 2.2$  Hz), 7.28–7.38 (m, 3H), 7.46 (d, 2H,  $J = 6.2$  Hz).  $^{13}\text{C}$  NMR:  $\delta$  20.4, 21.7, 30.9, 41.4, 76.1, 126.7, 126.8, 127.4, 127.7, 127.8, 127.9, 172.2. HRMS: calcd for  $\text{C}_{13}\text{H}_{13}\text{NO}$  [M] 199.0997, found 199.0998.

**2-Methyl-5-(1-phenyl-2-propynyl)furan:**<sup>6b</sup> pale yellow oil.  $^1\text{H}$  NMR:  $\delta$  2.23 (s, 3H), 2.41 (d, 1H,  $J = 3.0$  Hz), 5.00 (s, 1H), 5.88 (s, 1H), 6.06 (d, 1H,  $J = 3.0$  Hz), 7.25–7.43 (m, 5H).  $^{13}\text{C}$  NMR:  $\delta$  13.6, 37.0, 71.8, 82.3, 106.2, 107.4, 127.3, 127.7, 128.6, 138.5, 151.3, 152.0. Anal. Calcd for  $\text{C}_{14}\text{H}_{12}\text{O}$ : C, 85.68; H, 6.16. Found: C, 85.41; H, 5.88.

**5b:**<sup>1a</sup> pale yellow oil.  $^1\text{H}$  NMR:  $\delta$  1.26 (t, 3H,  $J = 7.2$  Hz), 2.31 (s, 6H), 2.83 (s, 1H), 3.52 (q, 2H,  $J = 7.2$  Hz), 7.10 (d, 4H,  $J = 7.6$  Hz), 7.42 (d, 4H,  $J = 7.6$  Hz).  $^{13}\text{C}$  NMR:  $\delta$  15.3, 21.0, 60.2, 76.8, 79.6, 83.9, 126.4, 128.8, 137.2, 140.7. IR (neat,  $\text{cm}^{-1}$ ): 2110 (C $\equiv$ C), 3287 ( $\equiv$ CH). Anal. Calcd for  $\text{C}_{19}\text{H}_{20}\text{O}$ : C, 86.32; H, 7.63. Found: C, 85.95; H, 7.51.

**5c:**<sup>1a</sup> pale yellow oil.  $^1\text{H}$  NMR:  $\delta$  1.27 (t, 3H,  $J = 7.2$  Hz), 2.86 (d, 1H,  $J = 2.0$  Hz), 3.54 (q, 2H,  $J = 7.2$  Hz), 7.22–7.33 (m, 6H), 7.56 (d, 4H,  $J = 8.0$  Hz).  $^{13}\text{C}$  NMR:  $\delta$  15.3, 60.4, 77.2, 79.9, 83.5, 126.5, 127.6, 128.1, 143.4. IR (neat,  $\text{cm}^{-1}$ ): 2110 (C $\equiv$ C), 3285 ( $\equiv$ CH). Anal. Calcd for  $\text{C}_{17}\text{H}_{16}\text{O}$ : C, 86.41; H, 6.82. Found: C, 85.97; H, 6.67.

**Preparation of Allenylidene Complexes [Cp\*RuCl( $\mu_2$ -YMe) $_2$ RuCp\*(C=C=CTol $_2$ )]OTf (Y = S, Se, Te).** A typical experimental procedure for the preparation of [Cp\*RuCl( $\mu_2$ -SMe) $_2$ RuCp\*(C=C=CTol $_2$ )]OTf (**1c**) is described below. In a 20 mL flask was placed **1b** (342 mg, 0.44 mmol) under N $_2$ . Anhydrous EtOH (10 mL) was added, and then the mixture was magnetically stirred at room temperature. After addition of 1,1-di-*p*-tolyl-2-propyn-1-ol (**4b**) (105 mg, 0.44 mmol), the reaction flask was kept at room temperature for 1 h. A precipitated purple solid was filtered off, washed with *n*-hexane, and recrystallized from CH $_2$ Cl $_2$ -*n*-hexane to give black crystals of **1c** (401 mg, 0.41 mmol, 93%).  $^1\text{H}$  NMR:  $\delta$  1.68 (s, 15H), 1.87 (s, 15H), 2.36 (s, 6H), 2.68 (s, 6H), 7.22 (d, 4H,  $J$  = 7.6 Hz), 7.54 (d, 4H,  $J$  = 7.6 Hz).  $^{13}\text{C}$  NMR:  $\delta$  10.4, 10.7, 19.6, 22.0, 98.8, 104.5, 129.9, 132.1, 140.4, 144.5, 162.2, 182.6, 296.6. IR (KBr, cm $^{-1}$ ): 1952 (C=C=C). Anal. Calcd for C $_{40}\text{H}_{50}\text{ClF}_3\text{O}_3\text{Ru}_2\text{S}_3$ : C, 49.55; H, 5.20. Found: C, 48.98; H, 5.31.

Spectroscopic data and isolated yield of other complexes are as follows.

**2c:** yield 94%; black crystals.  $^1\text{H}$  NMR:  $\delta$  1.70 (s, 15H), 1.88 (s, 15H), 2.35 (s, 6H), 2.57 (s, 6H), 7.21 (d, 4H,  $J$  = 8.0 Hz), 7.52 (d, 4H,  $J$  = 8.0 Hz).  $^{13}\text{C}$  NMR:  $\delta$  11.0, 11.3, 21.9, 96.6, 102.8, 129.4, 131.4, 140.2, 143.8, 162.0, 185.4, 298.1. IR (KBr,

cm $^{-1}$ ): 1933 (C=C=C). Anal. Calcd for C $_{40}\text{H}_{50}\text{ClF}_3\text{O}_3\text{Ru}_2\text{SSe}_2\cdot\text{CH}_2\text{Cl}_2$ : C, 42.88; H, 4.56. Found: C, 42.83; H, 4.56.

**3c:** yield 91%; black crystals.  $^1\text{H}$  NMR:  $\delta$  1.78 (s, 15H), 1.94 (s, 15H), 2.34 (s, 6H), 2.36 (s, 6H), 7.21 (d, 4H,  $J$  = 8.4 Hz), 7.58 (d, 4H,  $J$  = 8.4 Hz).  $^{13}\text{C}$  NMR:  $\delta$  12.4, 12.7, 95.1, 102.3, 129.3, 131.2, 140.7, 143.7, 164.5, 189.9, 298.5. IR (KBr, cm $^{-1}$ ): 1925 (C=C=C). Anal. Calcd for C $_{40}\text{H}_{50}\text{ClF}_3\text{O}_3\text{Ru}_2\text{STe}_2$ : C, 41.39; H, 4.34. Found: C, 41.52; H, 4.43.

**Acknowledgment.** This work was supported by a Grant-in-Aid for Scientific Research for Young Scientists (A) (No. 15685006) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. We also thank Dr. Izuru Takei of the Tokyo University of Science for assistance with cyclic voltammetry analysis.

**Supporting Information Available:** Text giving experimental procedures and tables and figures giving crystallographic data of **1a**, **1b**, **2a**, **2b**, **3a**, and **3b**; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM034137K