Synthesis and Reactivity of Hybrid Phosphido- and Thiolato-Bridged Diruthenium Complexes

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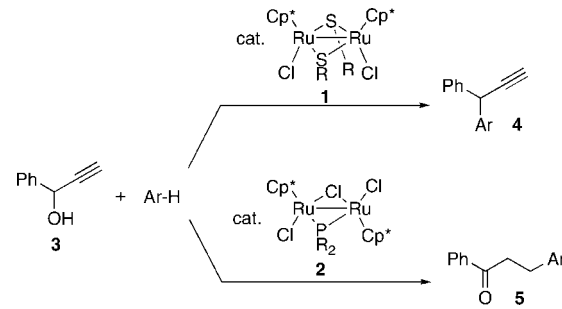
*Summary: Reactions of the monophosphido-bridged diruthenium(III) complexes [Cp*RuCl(μ-PR$_2$)(μ-Cl)RuClCp*] with a variety of (alkylthio)trimethylsilanes afford the hybrid phosphido- and thiolato-bridged diruthenium complexes [Cp*RuCl(μ-PR$_2$)(μ-SR′)RuClCp*]. Although some newly prepared hybrid diruthenium complexes are found to work as catalysts toward propargylic substitution reactions of propargylic alcohols with nucleophiles, their catalytic activity is lower than that of the methanethiolato-bridged diruthenium complex.*

Multimetallic complexes bridged by heteroatom ligands have attracted considerable attention as potentially useful catalysts for a variety of organic transformations, because the nature of the bridging ligands is expected to play an important role in the reactivity of multimetallic complexes.[1] We have already found a unique catalytic activity of the alkanethiolato-bridged diruthenium complexes [Cp*RuCl(μ-SR)]$_2$ (**1**) toward propargylic substitution reactions of propargylic alcohols with a variety of nucleophiles.[2,3] More recently, we have prepared the monophosphido-bridged diruthenium complexes [Cp*RuCl(μ-PR$_2$)(μ-Cl)RuClCp*] (**2**) and found a unique catalytic activity of the dimethylphosphido-bridged complex **2a** toward the redox isomerization of propargylic alcohols **3** followed by sequential Friedel−Crafts reaction with heteroaromatic compounds to give the β-arylated ketones **5** without any formation of the propargylated substituted product **4**. The result was in sharp contrast to the formation of **4** in the reaction of **3** with heteroaromatic compounds in the presence of a catalytic amount of **1** (Scheme 1).[4]

As an extension of our study on the preparation and reactivity of diruthenium complexes, we have now envisaged the preparation of diruthenium complexes bridged by other heteroatoms

Scheme 1



starting from **2**, because complexes **2** have a bridging chloride ligand which may be easily substituted with a variety of heteroatom ligands. Herein, we report a useful preparative method for the hybrid phosphido- and thiolato-bridged diruthenium complexes[5] from reactions of **2** with (alkylthio)- and (arylthio)trimethylsilanes and their catalytic activity toward propargylic substitution reactions of propargylic alcohols with nucleophiles.

Results and Discussion

Heating of **2a** with 1−3 equiv of (alkylthio)- and (arylthio)trimethylsilanes (R′S−SiMe$_3$) in tetrahydrofuran (THF) at 40 °C for 16 h gave the corresponding hybrid phosphido- and thiolato-bridged diruthenium complexes [Cp*RuCl(μ-PMe$_2$)(μ-SR')RuClCp*] (**6**: R′ = ^{i}Pr (**6a**), Bn (**6b**), Ph (**6c**)) in 70%, 68% and 55% yields, respectively (Scheme 2). Only the formation of *syn* isomers (*syn*-**6a** and *syn*-**6b**) was observed in the reactions with ^{i}PrS−SiMe$_3$ and BnS−SiMe$_3$, while only the *anti* isomer (*anti*-**6c**) was isolated in the reactions with PhS−SiMe$_3$. When the diethylphosphido-bridged complex **2b** was used as a precursor, the corresponding complex *syn*-**6d** was obtained in 42% yield. Next, the reaction of *syn*-**6a** with 1 equiv of silver trifluoromethanesulfonate (AgOTf; OTf = SO$_3$CF$_3$) in THF at room temperature for 16 h proceeded smoothly to give the corresponding monocationic diruthenium complex [Cp*Ru(μ-Cl)(μ-PR$_2$)(μ-S^{i}Pr)RuCp*]OTf ([**7**][OTf]) in 55% yield (Scheme 2).

These phosphido- and thiolato-bridged diruthenium complexes **6** and [**7**][OTf] were characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, and the molecular structures of *syn*-**6a** and *anti*-**6c** were confirmed by X-ray analysis. ORTEP drawings of *syn*-**6a** and *anti*-**6c** are shown in Figures 1 and 2, respectively.

(1) (a) *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Adams, R. D., Cotton, F. A., Eds.; Wiley-VCH: New York, 1998. (b) *Metal-Metal Bonds and Clusters in Chemistry and Catalysis*; Fackler, J. P., Ed.; Plenum: New York, 1990.

(2) For recent examples, see: (a) Nishibayashi, Y.; Uemura, S. *Curr. Org. Chem.* **2006**, *10*, 135. (b) Yamauchi, Y.; Onodera, G.; Sakata, K.; Yuki, M.; Miyake, Y.; Uemura, S.; Nishibayashi, Y. *J. Am. Chem. Soc.* **2007**, *129*, 5175. (c) Inada, Y.; Yoshikawa, M.; Milton, M. D.; Nishibayashi, Y.; Uemura, S. *Eur. J. Org. Chem.* **2006**, 881. (d) Nishibayashi, Y.; Shinoda, A.; Miyake, Y.; Matsuzawa, H.; Sato, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 4835. (e) Nishibayashi, Y.; Milton, M. D.; Inada, Y.; Yoshikawa, M.; Wakiji, I.; Hidai, M.; Uemura, S. *Chem. Eur. J.* **2005**, *11*, 1433. (f) Inada, Y.; Nishibayashi, Y.; Uemura, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 7715. (g) Ammal, S. C.; Yoshikai, N.; Inada, Y.; Nishibayashi, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2005**, *127*, 9428.

(3) (a) Nishibayashi, Y.; Imajima, H.; Onodera, G.; Hidai, M.; Uemura, S. *Organometallics* **2004**, *23*, 26. (b) Nishibayashi, Y.; Imajima, H.; Onodera, G.; Inada, Y.; Hidai, M.; Uemura, S. *Organometallics* **2004**, *23*, 5100.

(4) Miyake, Y.; Endo, S.; Nomaguchi, Y.; Yuki, M.; Nishibayashi, Y. *Organometallics* **2008**, *27*, 4017.

(5) For examples of phosphido- and thiolato-bridged diruthenium complexes, see: (a) Tschan, M. J.-L.; Chérioux, F.; Therrien, B.; Karmazin-Brelot, L.; Süss-Fink, G. *Acta Crystallogr.* **2006**, *E62*, m2916. (b) Cabeza, J. A.; Mulla, F.; Riera, V. *J. Organomet. Chem.* **1994**, *470*, 173.

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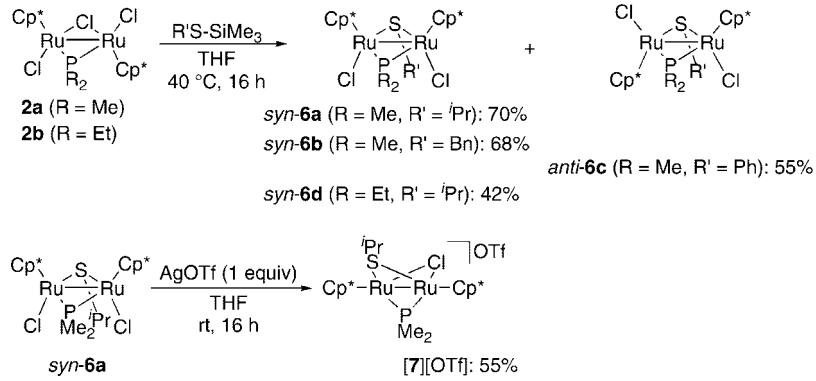
Scheme 2



The bond distances between the two ruthenium atoms in both **6a** and **6c** (2.8839(5) and 2.86682(15) Å) are slightly longer than that of the methanethiolate-bridged diruthenium complex $[Cp^*RuCl(\mu\text{-}SMe)]_2$ (**1a**) (2.8354(7) Å),[3a] but they are in accord with the generally known Ru−Ru single bond (2.71−3.02 Å).[6] On the other hand, the redox property of *syn*-**6a** was found to be quite different from that of **1**.[7] The cyclic voltammogram of *syn*-**6a** showed one reversible oxidation wave at $E_{1/2} = -0.08$ V and one irreversible oxidation wave at $E_{pa} = +0.92$ V, while that of **1a** exhibited two reversible oxidation waves at $E_{1/2} = -0.04$ and +0.89 V.[4] Bond distances and redox properties of *syn*-**6a** and **1a** are summarized in Table 1.

Next, we investigated the catalytic activities of **6** and [**7**][OTf] toward propargylic substitution reactions of propargylic alcohols with nucleophiles for comparison with that of **1a**. Typical results are shown in Table 2. Propargylation of 2-methylfuran with 1-phenyl-2-propyn-1-ol (**3**) in the presence of a catalytic amount

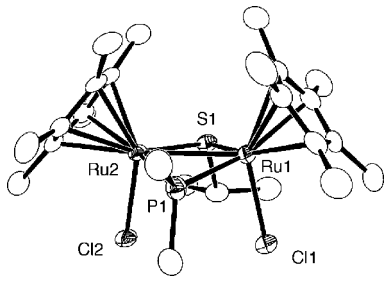


Figure 1. ORTEP drawing of *syn*-**6a**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): Ru1−Ru2, 2.8839(5); Ru1−P1, 2.2939(10); Ru2−P1, 2.2947(10); Ru1−S1, 2.3180(10); Ru2−S1, 2.3079(9); Ru1−Cl1, 2.4317(9); Ru2−Cl2, 2.4188(9).

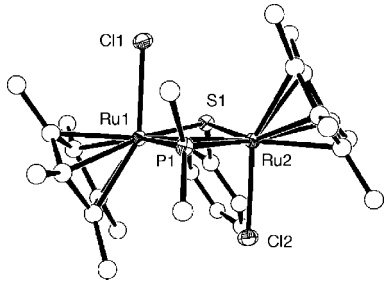
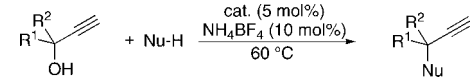


Figure 2. ORTEP drawing of *anti*-**6c**·THF. Hydrogen atoms and THF are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): Ru1−Ru2, 2.86682(15): Ru1−P1, 2.2894(4); Ru2−P1, 2.2857(4); Ru1−S1, 2.3410(4); Ru2−S1, 2.3258(4); Ru1−Cl1, 2.4614(5); Ru2−Cl2, 2.4462(5).

Table 1. Bond Distances and Redox Properties of 1a and *syn*-6a

	syn-**6a**	**1a**
Ru−Ru (Å)	2.8839(5)	2.8354(7)
oxidn potential (V)	−0.08 ($E_{1/2}$), +0.92 ($E_{p,a}$)	−0.04 ($E_{1/2}$), +0.89 ($E_{1/2}$)

Table 2. Propargylic Substitution Reactions of Propargylic Alcohols with Nucleophiles[a]



run	alcohol	Nu-H	cat	time (h)	product	yield (%)[b]
1[c]			**1a**	1		80
2[c]	Ph, OH, **3**	[d]	*syn*-**6a**	1	Ph, O, **4a**	26
3[c]			*syn*-**6b**	1		13
4[c]			*anti*-**6c**	1		0
5[c]			[**7**][OTf]	1		9
6[e]	*p*-tol, *p*-tol, OH, **8a**	EtOH	**1a**	20	*p*-tol, *p*-tol, OEt, **9a**	61
7[e]			*syn*-**6a**	20		36 (51)[f]

[a] All reactions of **3** or **8a** (0.60 mmol) with nucleophiles were carried out in the presence of a catalyst (5 mol %) and NH_4BF_4 (10 mol %). [b] Isolated yield. [c] $ClCH_2CH_2Cl$ was used as a solvent. [d] 2-Methylfuran (10 equiv) was used as a nucleophile. [e] Ethanol was used as a solvent. [f] For 36 h.

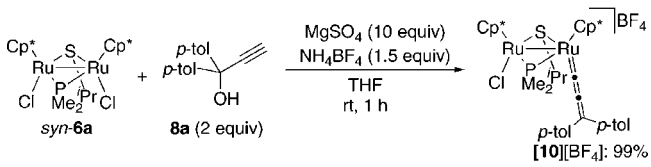
of *syn*-**6a**, *syn*-**6b**, and [**7**][OTf] gave the corresponding propargylated product (**4a**) in lower yields (Table 2, runs 2, 3, and 5). Unfortunately, *anti*-**6c** did not work as a catalyst for this reaction (Table 2, run 4). On the other hand, the reaction of 1,1-bis(4-methylphenyl)-2-propyn-1-ol (**8a**) with ethanol under the same reaction conditions proceeded slowly to give the corresponding propargylic ether (**9a**) (Table 2, run 6). A longer reaction time increased the yield of **9a** (Table 2, run 7). These results indicate that the newly prepared hybrid-bridged diruthenium complexes have a catalytic activity toward the propargylic substitution reactions, although their catalytic activity is lower than that of **1a**.

To obtain more information on the reaction pathway of the propargylic substitution reactions catalyzed by **6**, we have tried the isolation of the corresponding allenylidene complex and its stoichiometric reaction with alcohol. The reaction of *syn*-**6a** with 1 equiv of **8a** in the presence of 10 equiv of $MgSO_4$ and 1.5

(6) (a) Gao, Y.; Jennings, M. C.; Puddephatt, R. J.; Jenkins, H. A. *Organometallics* **2001**, *20*, 3500. (b) Engel, D. W.; Moodley, K. G.; Subramony, L.; Haines, R. J. *J. Organomet. Chem.* **1988**, *349*, 393, and references therein.

(7) A Pt stick as a working electrode and a Pt wire as a counter electrode were used in CH_2Cl_2 containing 0.1 M $^nBu_4NClO_4$ at room temperature. All potentials were measured against an Ag/Ag^+ reference electrode and converted to the values vs Fc/Fc^+.

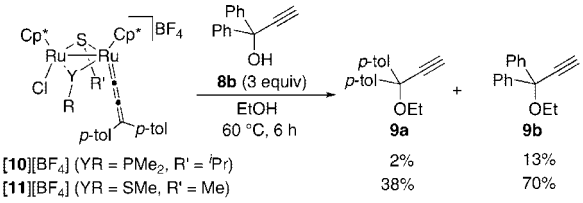
Scheme 3



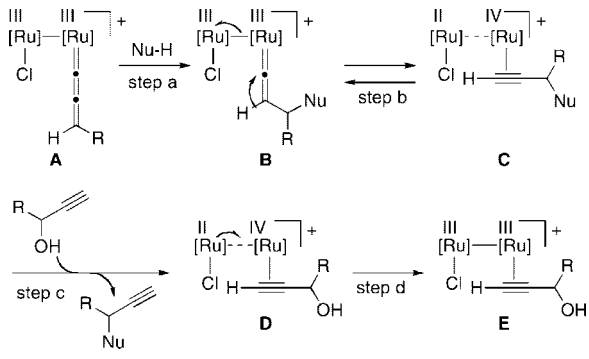
equiv of NH_4BF_4 in THF at room temperature for 1 h gave the corresponding allenylidene complex [**10**][BF_4] in 99% isolated yield (Scheme 3). The molecular structure of [**10**][BF_4] is supported by comparison of the spectral data with those of the allenylidene complex [**11**][BF_4] derived from **1a** and **8a**. Treatment of [**10**][BF_4] with EtOH in the presence of 3 equiv of 1,1-diphenyl-2-propyn-1-ol (**8b**) at 60 °C for 6 h afforded **9a** in only 2% yield together with **9b** in 13% yield (Scheme 4). This result was in sharp contrast to the stoichiometric reaction of the allenylidene complex [**11**][BF_4], where both **9a** and **9b** were obtained in much higher yield.[2e,3]

Previously, we proposed the reaction pathway for the propargylic substitution reaction catalyzed by **1**, as shown in Scheme 5.[3] Results in Scheme 4 may indicate that, in the case of *syn*-**6a**, either the step of a nucleophilic attack to **A** (step a in Scheme 5) does not proceed smoothly or the ligand exchange with another propargylic alcohol (step c in Scheme 5) does not occur readily. The difficulty of the charge transfer between two ruthenium atoms in the hybrid complex *syn*-**6a** may correspond to its lower catalytic activity.[8]

Scheme 4



Scheme 5



In summary, a variety of hybrid phosphido- and thiolato-bridged diruthenium complexes were newly prepared from the monophosphido-bridged diruthenium complexes, which are useful precursors for the diruthenium complexes bridged by different heteroatoms. Although the produced phosphido- and thiolato-bridged diruthenium complexes were found to work as catalysts for the propargylic substitution reactions of propargylic alcohols with nucleophiles, their catalytic activity was lower than that of the dithiolato-bridged complexes. These results revealed that the nature of bridging ligands has a remarkable effect on their catalytic activity. We believe that the result described in this paper may provide a new concept to design polynuclear transition-metal complexes useful for organic transformations. Further work is currently in progress to prepare other hybrid heteroatom-bridged diruthenium complexes.

(8) We have previously reported that the bond distances between two ruthenium atoms in a variety of chalcogenolato-bridged diruthenium complexes have an effect on the charge transfer, which seems to be a key step in promoting propargylic substitution reactions.[3]

Experimental Section

General Considerations. ^{1}H NMR (270 MHz) and ^{31}P NMR (109 MHz) spectra were recorded on a JEOL Excalibur 270 spectrometer in a suitable solvent. Elemental analyses were performed at the Microanalytical Center of The University of Tokyo. Mass spectra were measured on a JEOL JMS-700 mass spectrometer. All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by the usual methods and distilled before use. Monophosphido-bridged diruthenium complexes[Cp*RuCl(μ-PR_2)(μ-Cl)RuClCp*] (**2**) were prepared according to the literature procedures.[4] The propargylic substituted products **4a**, **9a**, and **9b** and the allenylidene complex [**11**][BF_4] are known compounds.[2e]

Preparation of Phosphido- and Thiolato-Bridged Diruthenium(III) Complexes 6. A typical experimental procedure for **6a** is described below. To a solution of diisopropyl disulfide (112.7 mg, 0.75 mmol) in THF (3.0 mL) was added sodium metal (34.5 mg, 1.5 mmol), and the mixture was stirred at room temperature. After 16 h, a solution of chlorotrimethylsilane (179.3 mg, 1.7 mmol) in THF (1.0 mL) was added, and the mixture was stirred for an additional 1 h. To the resulting solution were added [Cp*RuCl(μ_2-Cl)(μ_2-PMe_2)RuClCp*] (**2a**; 327.3 mg, 0.51 mmol) and THF (5.0 mL), and the mixture was stirred at 40 °C for 16 h. The solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 (50 mL). The extract was filtered through Celite under a nitrogen atmosphere, and the filtrate was concentrated under reduced pressure. The residue was recrystallized from CH_2Cl_2−*n*-hexane to give dark red needles of **6a** (244.2 mg, 0.36 mmol, 70%). ^{1}H NMR (CD_2Cl_2): δ 1.32 (d, 6H, J = 6.8 Hz), 1.62−1.68 (m, 33H), 2.16 (d, 3H, J = 10.5 Hz), 4.12 (sep, 1H, J = 6.8 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 211.4 (s). Anal. Calcd for $C_{25}H_{43}Cl_2PRu_2S$: C, 44.18; H, 6.38. Found: C, 43.90; H, 6.32.

Dimethylphosphido- and Phenylmethanethiolato-Bridged Diruthenium(III) Complex 6b. Yield: 68%. Dark red blocks. ^{1}H NMR (CD_2Cl_2): δ 1.55 (d, 30H, J = 0.81 Hz), 1.72 (d, 3H, J = 11.6 Hz), 2.12 (d, 3H, J = 10.5 Hz), 3.97 (s, 2H), 7.18−7.57 (m, 5H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 214.0 (s). Anal. Calcd for $C_{29}H_{43}Cl_2PRu_2S$: C, 47.86; H, 5.96. Found: C, 48.08; H, 5.96.

Dimethylphosphido- and Benzenethiolato-Bridged Diruthenium(III) Complex 6c. Yield: 55%. Dark red blocks. ^{1}H NMR (CD_2Cl_2): δ 1.59 (d, 30H, J = 0.81 Hz), 2.36 (d, 3H, J = 12.2 Hz), 2.62 (d, 3H, J = 11.1 Hz), 7.20−7.34 (m, 5H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 264.3 (s). HRMS: *m*/*z* calcd for $C_{28}H_{41}ClPRu_2S$ [M − Cl] 679.0452, found 679.0460.

Diethylphosphido- and 2-Propanethiolato-Bridged Diruthenium(III) Complex 6d. Yield: 42%. Dark red blocks. ^{1}H NMR (CD_2Cl_2): δ 1.09−1.21 (m, 3H), 1.31−1.38 (m, 9H), 1.62 (d, 30H, J = 0.81 Hz), 2.20−2.49 (m, 4H), 4.10 (sep, 1H, J = 6.95 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 241.8 (s). Anal. Calcd for $C_{27}H_{47}Cl_2PRu_2S$: C, 45.82; H, 6.69. Found: C, 45.76; H, 6.61.

Preparation of Cationic Dimethylphosphido- and 2-Propanethiolato-Bridged Diruthenium(III) Complex [7][OTf]. To a solution of **6a** (135.7 mg, 0.20 mmol) in THF (3 mL) was added AgOTf (51.5 mg, 0.20 mmol), and the mixture was stirred at room temperature for 16 h. The solvent was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered through Celite under a nitrogen atmosphere, and the filtrate was concentrated under reduced pressure. The residue was recrystallized from acetone−Et_2O to

give dark red blocks of [**7**][OTf] (88.9 mg, 0.11 mmol, 55%). Major isomer: ^{1}H NMR (CD_2Cl_2) δ 1.04 (d, 6H, J = 7.0 Hz), 1.80 (d, 30H, J = 1.4 Hz), 2.34 (d, 3H, J = 12.4 Hz), 2.39 (d, 3H, J = 10.8 Hz), 2.65 (sep, 1H, J = 7.0 Hz); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 270.3 (s). Minor isomer: ^{1}H NMR (CD_2Cl_2) δ 1.54 (d, 6H, J = 7.0 Hz), 1.74 (d, 30H, J = 1.4 Hz), 2.06 (d, 3H, J = 11.3 Hz), 2.52 (d, 3H, J = 11.1 Hz), 3.73 (sep, 1H, J = 7.0 Hz); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 270.3 (s). Anal. Calcd for $C_{26}H_{43}ClF_3O_3PRu_2S_2$: C, 39.36; H, 5.46. Found: C, 39.33; H, 5.33.

Preparation of [Cp*RuCl(μ-PMe$_2$)(μ-S^{i}Pr)Ru(Cp*)(C=C=C-(*p*-tol)$_2$)]BF$_4$ ([10][BF$_4$]). The phosphido- and thiolato-bridged complex *syn*-**6a** (102 mg, 0.15 mmol), NH_4BF_4 (20.2 mg, 0.19 mmol), and $MgSO_4$ (185.5 mg) were placed in a 50 mL flask under N_2. Anhydrous THF (20 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of 1,1-bis(4-methylphenyl)-2-propyn-1-ol (**8a**; 73.1 mg, 0.31 mmol), the reaction flask was kept at room temperature for 1 h. Then, the solvent was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered through Celite under a nitrogen atmosphere, and the filtrate was concentrated under reduced pressure. The residue was recrystallized from toluene/pentane to give a dark purple solid of [**10**][BF_4] (142.4 mg, 0.15 mmol, 99%). ^{1}H NMR (CD_2Cl_2): δ 1.25 (d, 3H, J = 7.0 Hz), 1.32 (d, 3H, J = 6.8 Hz), 1.71 (s, 15H), 1.72 (d, 3H, J = 11.1 Hz), 1.85 (s 15H), 2.20 (d, 3H, J = 10.8 Hz), 2.35 (s, 6H), 4.07 (sep, 1H, J = 7.8 Hz), 7.21 (d, 4H, J = 7.8 Hz), 7.57 (d, 4H, J = 8.1 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 225.8 (s). Anal. Calcd for $C_{42}H_{57}BClF_4PRu_2S$: C, 53.14; H, 6.05. Found: C, 52.96; H, 6.30.

Ruthenium-Catalyzed Propargylation of 2-Methylfuran with Propargylic Alcohol. A typical experimental procedure for the reaction of 2-methylfuran with 1-phenyl-2-propyn-1-ol (**3**) in the presence of **6a** is described below. In a 20 mL flask were placed *syn*-**6a** (20.5 mg, 0.03 mmol) and NH_4BF_4 (6.0 mg, 0.06 mmol) under N_2. Anhydrous and degassed 1,2-dichloroethane (15.0 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of 1-phenyl-2-propyn-1-ol (**3**; 78.8 mg, 0.60 mmol) and 2-methylfuran (493 mg, 6.0 mmol), the reaction flask was kept at 60 °C for 1 h. The resulting mixture was filtered through Florisil and Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, eluent *n*-hexane/ethyl acetate 20/1) to give **4a** (30.8 mg, 0.157 mmol, 26% yield) as a yellow oil.[2e] ^{1}H NMR ($CDCl_3$): δ 2.23 (s, 3H), 2.41 (d, 1H, J = 2.7 Hz), 4.99 (s, 1H), 5.88 (s, 1H), 6.06 (d, 1H, J = 3.0 Hz), 7.24−7.43 (m, 5H).

Ruthenium-Catalyzed Reaction of Propargylic Substitution Reactions of Propargyl Alcohol with EtOH. A typical experimental procedure for the reaction of 1-bis(4-methylphenyl)-2-propyn-1-ol (**8a**) with EtOH catalyzed by *syn*-**6a** is described below. In a 20 mL flask were placed *syn*-**6a** (20.6 mg, 0.03 mmol) and NH_4BF_4 (6.4 mg, 0.06 mmol) under N_2. Anhydrous and degassed EtOH (15.0 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of 1,1-bis(4-methylphenyl)-2-propyn-1-ol (**8a**; 141.6 mg, 0.60 mmol), the reaction flask was kept at 60 °C for 20 h. The resulting mixture was filtered through Florisil and Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, eluent *n*-hexane/ethyl acetate 20/1) to give **9a** (56.5 mg, 0.214 mmol, 36% yield) as a yellow oil.[2e] ^{1}H NMR ($CDCl_3$): δ 1.25 (t, 3H, J = 7.0 Hz), 2.30 (s, 6H), 2.82 (s, 1H), 3.52 (q, 2H, J = 7.0 Hz), 7.10 (d, 4H, J = 8.4 Hz), 7.43 (d, 4H, J = 8.4 Hz).

Table 3. Summary of Crystallographic Data.

	syn-**6a**	*anti*-**6c**·THF
formula	$C_{25}H_{43}PSCl_2Ru_2$	$C_{32}H_{49}OPSCl_2Ru_2$
fw	679.69	785.82
cryst size/mm	0.50 × 0.25 × 0.20	0.35 × 0.30 × 0.25
color, habit	brown, block	dark brown, block
cryst syst	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a/Å	17.0596(7)	10.5851(4)
b/Å	8.9122(3)	12.3136(7)
c/Å	18.6207(7)	13.1597(7)
α/deg		78.4177(17)
β/deg	93.9558(14)	81.6515(15)
γ/deg		89.9665(16)
V/Å^3	2824.32(18)	1661.78(14)
Z	4	2
d_c/g cm^{-3}	1.598	1.570
μ(Mo Kα)/cm^{-1}	14.011	12.047
no. of data collected	23 756	16 605
no. of unique data	6352 (R_{int} = 0.040)	7556 (R_{int} = 0.016)
R1[a] ($I > 2\sigma$(I))	0.0322	0.0220
wR2[b]	0.0761	0.0494
goodness of fit indicator[c]	1.050	1.000
largest shift/esd, final cycle	0.000	0.000
residual electron density/e Å^{-3}	+1.96/−1.25	+0.72/−0.66

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, where $w = 1/[pF_o^2 + q\sigma(F_o^2)]/(4F_o^2)$ (p = 0.0003 (*syn*-**6a**), 0 (*anti*-**6c**·THF); q = 1.0000 (*syn*-**6a**), 2.7450 (*anti*-**6c**·THF)). [c] $[\sum w(F_o^2 - F_c^2)^2/(N_{observns} - N_{params})]^{1/2}$.

X-ray Crystallography. Crystallographic data for *syn*-**6a** and *anti*-**6c** are summarized in Table 3. The crystals were immersed in immersion oil (Sigma-Aldrich, Cat. Code I0890) on a nylon loop and mounted on a Rigaku RAXIS RAPID imaging plate. Data were collected at −100 °C under a cold nitrogen stream using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Empirical absorption corrections were applied. Structures were solved by direct methods[9] and refined on F^2 by full-matrix least squares using the Crystal Structure software package.[10] Anisotropic thermal parameters were introduced for all non-hydrogen atoms. All hydrogen atoms were generated at calculated positions (d_{C-H} = 0.97 Å) and treated as riding atoms with isotropic thermal factors. Crystallographic data are also given in a CIF file in the Supporting Information.

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Supporting Information Available: CIF files giving X-ray crystallographic data for *syn*-**6a** and *anti*-**6c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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