Preparation of Alkanechalcogenolate- and Benzenechalcogenolate-Bridged Diruthenium Complexes and Their Catalytic Activity toward Propargylation of Acetone with Propargylic Alcohol

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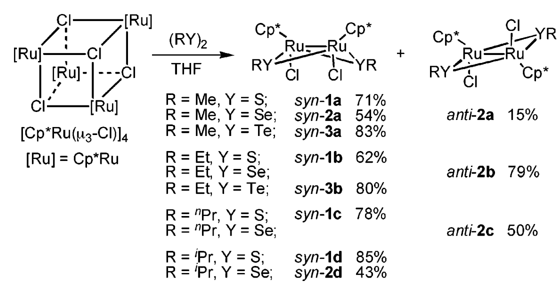
Summary: Various alkanechalcogenolate (SR, SeR, TeR)- and benzenechalcogenolate (SPh, SePh, TePh)-bridged diruthenium complexes have been newly prepared, and their catalytic activity toward the propargylation of acetone with propargylic alcohol has been investigated for comparison. Ab initio molecular orbital calculations of syn and anti methanechalcogenolate-bridged, propane-2-selenolate-bridged, and benzenethiolate-bridged diruthenium complexes have been carried out to explain the reason for favorable formation of either isomer.

Introduction

We have recently found that the efficient ruthenium-catalyzed propargylic substitution reactions of propargylic alcohols with various heteroatom- and carbon-centered nucleophiles gave the corresponding propargylated products in high yields with complete regioselectivity.[1] It is noteworthy that the reactions are catalyzed by thiolate-bridged diruthenium complexes such as $[Cp^*RuCl(\mu_2\text{-}SR)]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$; R = Me, ^{n}Pr, ^{i}Pr) and $[Cp^*RuCl(\mu_2\text{-}SMe)_2RuCp^*(OH_2)]OTf$ (OTf = OSO_2CF_3), but not by various monoruthenium complexes.[2] More recently, we have prepared a series of methanechalcogenolate-bridged diruthenium complexes and compared their catalytic activities toward propargylic substitution reactions.[3] As a result, it was revealed that thiolate- and selenolate-bridged diruthenium complexes were quite effective as catalysts, while tellurolate-bridged complexes did not show any catalytic activity.[3] During these investigations we came across the phenomenon that these diruthenium complexes could be formed in two stereoisomeric forms, *syn* and *anti*, the ratio depending greatly on the kind of organic group on chalcogen as well as that of chalcogen atoms. This finding prompted us to investigate a whole aspect of the preparation and catalytic reactivity of a variety of organochalcogenolate-bridged diruthenium complexes, supported by an unambiguous X-ray structural determination of the new complexes prepared. We describe here in detail the preparation of a variety of *syn* and *anti* alkanechalcogenolate- and benzenechalcogenolate-bridged diruthenium complexes together with the result of ab initio molecular orbital calculations on the stability of some complexes and also the result of the propargylation of acetone with propargylic alcohol catalyzed by these diruthenium complexes.

Scheme 1



Results and Discussion

$[Cp^*RuCl(\mu_2\text{-}SeMe)]_2$ (*syn*-**2a**)[3] was isolated in 54% yield from the reaction of the tetranuclear ruthenium(II) complex $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ with dimethyl diselenide in tetrahydrofuran (THF) at room temperature for 20 h. By careful examination of the filtrate after recrystallization of *syn*-**2a**, the presence of another diruthenium complex was disclosed, and it was actually isolated in 16% yield. This was revealed to be the *anti* methaneselenolate-bridged diruthenium complex $[Cp^*RuCl(\mu_2\text{-}SeMe)]_2$ (*anti*-**2a**) by X-ray analysis (Scheme 1). The ORTEP drawing of *anti*-**2a** is shown in Figure 1, which clearly shows the presence of the doubly bridged μ_2-SeMe moieties and that of the two Cp* groups and two chloride ligands in a *trans* configuration relative to one another. Similarly, methanethiolate- and methanetellurolate-bridged diruthenium complexes, $[Cp^*RuCl(\mu_2\text{-}SMe)]_2$ (*syn*-**1a**) and $[Cp^*RuCl(\mu_2\text{-}TeMe)]_2$

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(1) (a) Nishibayashi, Y.; Wakiji, I.; Hidai, M. *J. Am. Chem. Soc.* **2000**, *122*, 11019. (b) Nishibayashi, Y.; Wakiji, I.; Ishii, Y.; Uemura, S.; Hidai, M. *J. Am. Chem. Soc.* **2001**, *123*, 3393. (c) Inada, Y.; Nishibayashi, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 15172. (d) Nishibayashi, Y.; Onodera, G.; Inada, Y.; Hidai, M.; Uemura, S. *Organometallics* **2003**, *22*, 873.

(2) (a) 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. (b) The methanethiolate-bridged diruthenium complex $[Cp^*RuCl(\mu_2\text{-}SMe)_2RuCp^*Cl]$ (*syn*-**1a**) is commercially available from Wako Pure Chemical Industries (Japan) as met-DIRUX (*met*hanethiolate-bridged *diru*thenium comple*x*) (No. 130-14581).

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

10.1021/om049475f CCC: $27.50
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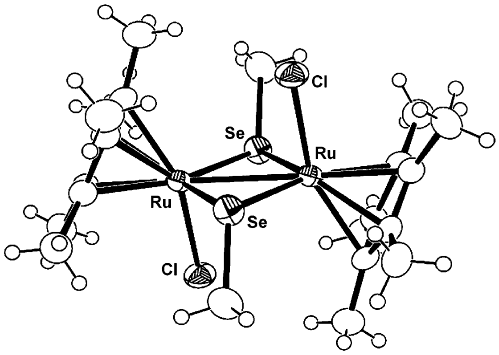


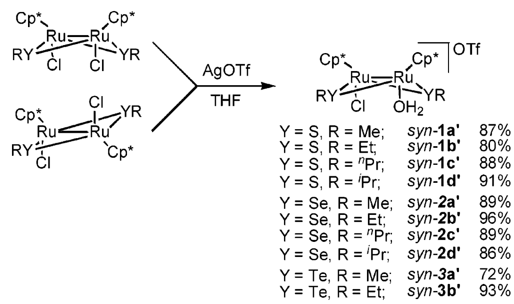
Figure 1. Crystal structure of *anti*-[Cp*RuCl(μ_2-SeMe)]$_2$ (*anti*-**2a**) with 50% probability ellipsoids.

(*syn*-**3a**), were prepared by using dimethyl disulfide and dimethyl ditelluride in 71% and 83% isolated yields, respectively (Scheme 1).[3] In these cases the preparation of a very minor amount of another diruthenium complex, which was thought to be the *anti* isomer, was detected but could not be isolated. It has been previously confirmed that no isomerization occurred between these isomers when a mixture of *syn* and *anti* thiolate-bridged diruthenium complexes was heated at 60 °C for 5 h.[1d]

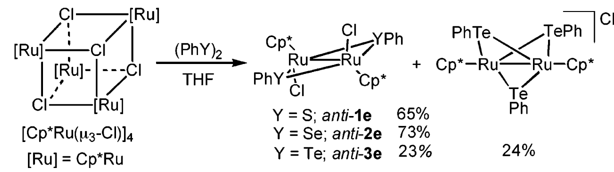
When the reactions of the tetranuclear ruthenium(II) complex [Cp*Ru(μ_3-Cl)]$_4$ with other dialkyl dichalcogenides were carried out under similar reaction conditions, the corresponding alkanechalcogenolate-bridged diruthenium complexes [Cp*RuCl(μ_2-YR)]$_2$ were obtained in good to high isolated yields, the yields of the complexes being shown in Scheme 1. In contrast to the formation of *syn* alkanethiolate (*syn*-**1b**,[4] *syn*-**1c**, *syn*-**1d**)-, *syn* alkanetellurolate (*syn*-**3b**)-, and *syn* propane-2-selenolate (*syn*-**2d**)-bridged diruthenium complexes, only the *anti* isomer was formed in the cases of ethaneselenolate- and *n*-propaneselenolate-bridged diruthenium complexes (*anti*-**2b** and *anti*-**2c**). The ORTEP drawings of *anti*-**2b**, *syn*-**3b**, *anti*-**2c**, and *syn*-**2d** are shown in the Supporting Information (Figures S2−S5, respectively).

Treatment of the neutral alkanechalcogenolate-bridged diruthenium complexes obtained thus far with an equimolar amount of silver triflate (AgOTf)[1c,d,5] in THF at room temperature for 1 h gave the corresponding cationic alkanechalcogenolate-bridged diruthenium complexes [Cp*RuCl(μ_2-YR)$_2$RuCp*(OH$_2$)]OTf (Y = S, Se, Te; R = Me,[3] Et, ^{n}Pr, ^{i}Pr) in high yields with complete stereoselectivity (Scheme 2). For instance, the reaction of either *syn*-**2a** or *anti*-**2a** with AgOTf gave the same cationic complex, [Cp*RuCl(μ_2-SeMe)$_2$RuCp*(OH$_2$)]OTf (*syn*-**2a′**), in 89% or 77% isolated yield, respectively, as a single isomer. Although anhydrous solvents were used, the cationic complexes contain a water molecule as a ligand, probably due to adventitious water in the solvents. Similarly, starting from either the *syn* or *anti* isomer of either diruthenium complex, only the cationic *syn* isomer was obtained in all cases, in which only the molecular structures of *syn*-**2b′** and *syn*-**2d′** were unambiguously determined by X-ray analysis (Supporting Information, Figures S6 and S7). The

Scheme 2



Scheme 3



intramolecular distances between the two ruthenium atoms (2.84−3.06 Å) correspond to a Ru−Ru single bond (2.71−3.02 Å).[6] The Ru−Ru bond distances of the cationic complexes were slightly shorter than those of the neutral complexes. The selected bond lengths and angles for these complexes are shown in the Supporting Information (Table S11). The orientations of the chalcogenolate substituents are almost the same in all cases.

Although the preparation of ferrocenechalcogenolate-bridged diruthenium complexes [Cp*RuCl(μ_2-YFc)]$_2$ (Y = S, Se, Te; Fc = ferrocenyl) has already been reported by our group,[7] other arenechalcogenolate-bridged diruthenium complexes [Cp*RuCl(μ_2-YAr)]$_2$ (Y = S, Se, Te; Ar = aryl) have not yet been prepared until now. Treatment of the tetranuclear ruthenium(II) complex [Cp*Ru(μ_3-Cl)]$_4$ with diphenyl disulfide and diselenide in THF at room temperature for 20 h gave the benzenethiolate- and benzeneselenolate-bridged diruthenium complexes [Cp*RuCl(μ_2-YPh)]$_2$ (**1e** (Y = S) and **2e** (Y = Se)) in 65% and 73% isolated yields, where the formation of only *anti* isomers was observed, in sharp contrast to the alkanethiolate case (Scheme 3). The molecular structures of the complex (*anti*-**1e** and *anti*-**2e**) were unambiguously confirmed by X-ray analysis, and ORTEP drawings are shown in the Supporting Information (Figures S8 and S9). In the reaction with diphenyl ditelluride, the corresponding benzenetellurolate-bridged diruthenium complex [Cp*RuCl(μ_2-TePh)]$_2$ (*anti*-**3e**) was formed in only 23% isolated yield, together with the diruthenium complex [Cp*Ru(μ_2-TePh)$_3$RuCp*]Cl[8] (24% isolated yield), although the molecular structures of these complexes could not be determined by X-ray analysis (Scheme 3).

Interestingly, treatment of the neutral benzenethiolate-bridged diruthenium complex (*anti*-**1e**) with an

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(8) (a) A similar benzenethiolate-bridged complex, [Cp*Ru(μ_2-SPh)$_3$RuCp*]Cl, has already been reported; Dev, S.; Imagawa, K.; Mizobe, Y.; Cheng, G.; Wakatsuki, Y.; Yamazaki, H.; Hidai, M. *Organometallics* **1989**, *8*, 1232. (b) Matsuzaka, H.; Ogino, T.; Nishio, M.; Hidai, M.; Nishibayashi, Y.; Uemura, S. *J. Chem. Soc., Chem. Commun.* **1994**, 223.

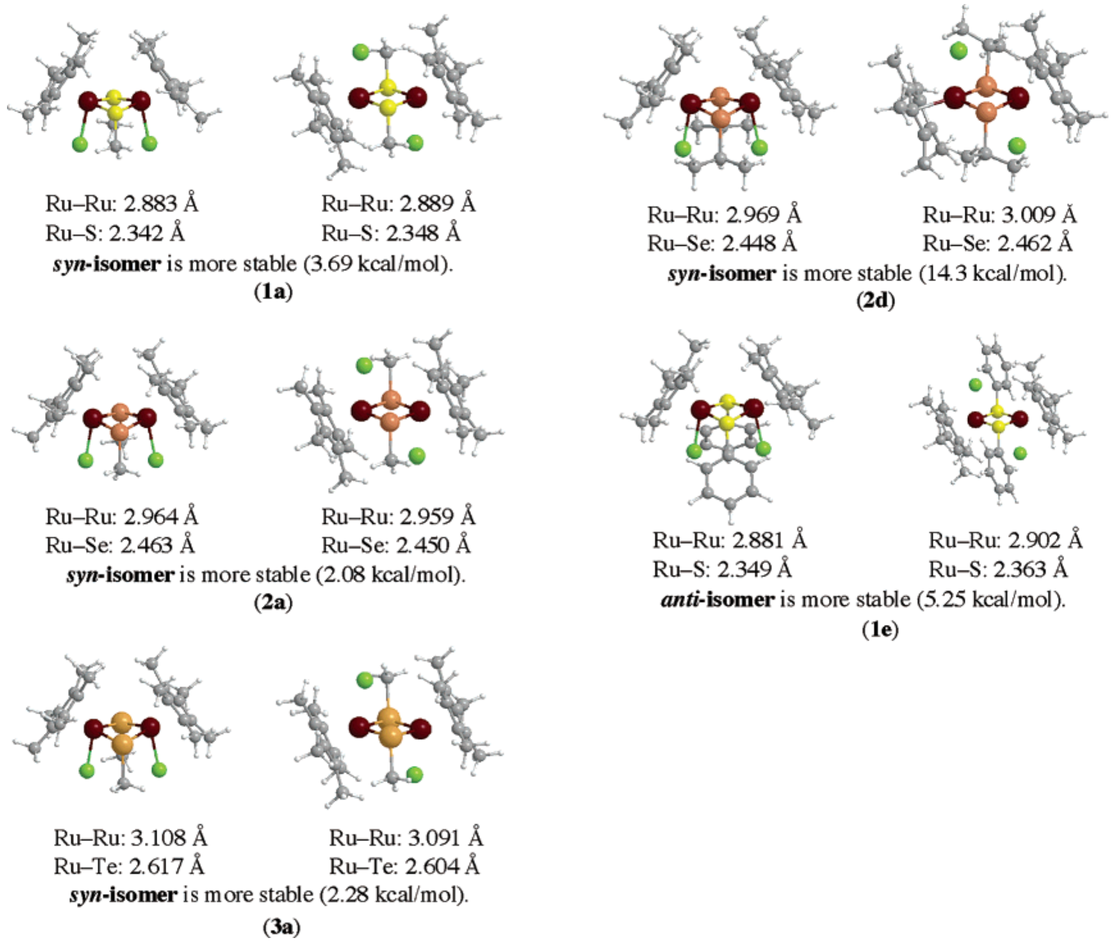
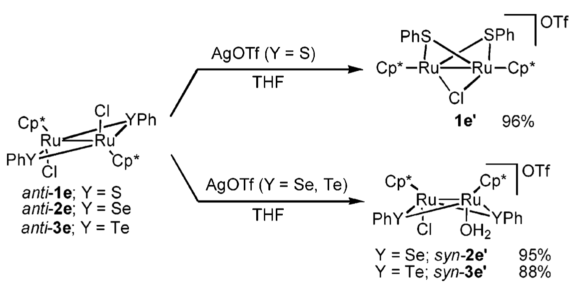


Figure 2. Molecular structures of [Cp*RuCl(μ_2-SMe)]$_2$ (**1a**), [Cp*RuCl(μ_2-SeMe)]$_2$ (**2a**), [Cp*RuCl(μ_2-TeMe)]$_2$ (**3a**), [Cp*RuCl(μ_2-Se^{i}Pr)]$_2$ (**2d**), and [Cp*RuCl(μ_2-SPh)]$_2$ (**1e**).

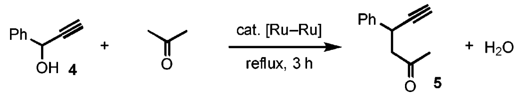
Scheme 4



equimolar amount of AgOTf in THF at room temperature for 1 h gave the corresponding cationic benzenethiolate-bridged diruthenium complex [Cp*Ru(μ_2-Cl)(μ_2-SPh)$_2$RuCp*]OTf (**1e′**) in 96% isolated yield as a single isomer (Scheme 4). The molecular structure of the complex (**1e′**) was unambiguously determined by X-ray analysis, and an ORTEP drawing is shown in the Supporting Information (Figure S10). The dinuclear structure of **1e′** is bridged by one chloride moiety and two benzenethiolate moieties, the latter of which are present in a cis configuration. The Ru−Ru bond distance of **1e′** is apparently shorter than those of other cationic alkanethiolate-bridged diruthenium complexes. Similarly, the corresponding cationic benzeneselenolate- and benzenetellurolate-bridged diruthenium complexes [Cp*RuCl(μ_2-YPh)$_2$RuCp*]OTf (**2e′** (Y = Se) and **3e′** (Y = Te)) were obtained in 95% and 88% isolated yields, respectively, but their molecular structures are not the same as that of **1e′** and considered to have a *syn* configuration of benzenechalcogenolate moieties (Scheme 4), similar to the corresponding cationic *syn* complexes produced in the reactions of the corresponding ferrocenechalcogenolate-bridged diruthenium complexes with AgOTf.[7]

Ab initio molecular orbital calculations of the methanechalcogenolate-bridged, propane-2-selenolate-bridged, and benzenethiolate-bridged diruthenium complexes (**1a**, **2a**, **3a**, **2d**, and **1e**) were carried out to find the reason for the favorable formation of either syn or anti isomers. As shown in Figure 2, the structural optimizations gave quite similar geometries to those of X-ray analysis. The energies of all complexes were obtained by the single-point enegy calculations for optimized geometries. Figure 2 shows the relative energy differences for *syn* and *anti* methanechalcogenolate-bridged diruthenium complexes (**1a**, **2a**, and **3a**), propane-2-selenolate-bridged diruthenium complexes (**2d**), and benzenethiolate-bridged diruthenium complexes (**1e**). In general, *syn* methanechalcogenolate-bridged diruthenium complexes (*syn*-**1a**, *syn*-**2a**, and *syn*-**3a**) are more stable than the corresponding anti complexes (*anti*-**1a**, *anti*-**2a**, and *anti*-**3a**), the calculated energy differences between *syn* and *anti* complexes being 3.69, 2.08, and 2.28 kcal/mol, respectively. Steric repulsion between the Cp* ring and the bridged alkane moiety of the *anti* complex is considered to be the reason the *syn* complex is more stable than the *anti* complex. In contrast, the *anti* benzenethiolate-bridged diruthenium complex (*anti*-

Table 1. Propargylation of Acetone with 4 Using a Diruthenium Complex as Catalyst[a]



run	R	Y	complex	yield (%)[b]	run	R	Y	complex	yield (%)[b]
1	Me	S	*syn*-**1a**	88	15[c]	Me	S	*syn*-**1a′**	93[d,e]
2	Me	Se	*syn*-**2a**	95	16[c]	Me	Se	*syn*-**2a′**	95[d,e]
3	Me	Se	*anti*-**2a**	0	17[c]	Me	Te	*syn*-**3a′**	0[d,e]
4	Me	Te	*syn*-**3a**	0	18[c]	Et	S	*syn*-**1b′**	90
5	Et	S	*syn*-**1b**	90	19[c]	Et	Se	*syn*-**2b′**	89
6	Et	Se	*anti*-**2b**	50	20[c]	Et	Te	*syn*-**3b**	5
7	Et	Te	*syn*-**3b**	0	21[c]	^{n}Pr	S	*syn*-**1c′**	94
8	^{n}Pr	S	*syn*-**1c**	84	22[c]	^{n}Pr	Se	*syn*-**2c′**	90
9	^{n}Pr	Se	*anti*-**2c**	32	23[c]	^{i}Pr	S	*syn*-**1d′**	93
10	^{i}Pr	S	*syn*-**1d**	84	24[c]	^{i}Pr	Se	*syn*-**2d′**	92
11	^{i}Pr	Se	*syn*-**2d**	61	25[c]	Ph	S	**1e′**	0
12	Ph	S	*anti*-**1e**	0	26[c]	Ph	Se	*syn*-**2e**	0
13	Ph	Se	*anti*-**2e**	0	27[c]	Ph	Te	*syn*-**3e**	0
14	Ph	Te	*anti*-**3e**	0					

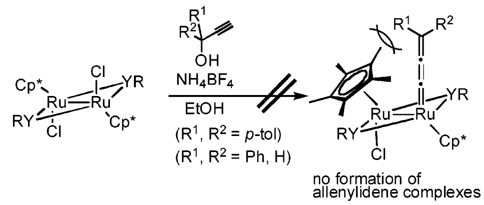
[a] All the reactions of propargylic alcohol (**4**; 0.60 mmol) with acetone (36 mL) in the presence of complex (0.03 mmol) and NH_4BF_4 (0.06 mmol) at reflux for 3 h. [b] Isolated yield of **5**. [c] Without NH_4BF_4. [d] Complex (2.5 mol %) was used. [e] GLC yield of **5**.

1e) is more stable than the corresponding *syn* complex, the calculated energy difference between *syn* and *anti* complexes being 5.25 kcal/mol. Experimental results of the formation of these complexes are consistent with the density functional calculations. The reason the formation of two isomers was observed in the case of methaneselenolate-bridged diruthenium complexes (**2a**) is considered to be due to the relatively lower energy difference between *syn* and *anti* complexes. In fact, the *syn* propaneselenolate-bridged diruthenium complex *syn*-**2d** is more stable than the corresponding *anti* complex, the calculated energy difference between *syn* and *anti* complexes being 14.3 kcal/mol. This is consistent with the experimental result of only *syn* complex formation. Thus, the thermodynamic stability of the complexes is the most important factor in determining the stereoselectivity of the complexes formed in the reactions of the tetranuclear ruthenium(II) complex [Cp*Ru(μ_3-Cl)]$_4$ with dialkyl and diphenyl dichalcogenides.

Next, the catalytic reactivity of various chalcogenolate-bridged diruthenium complexes toward the propargylation[1b,d,3] of acetone with propargylic alcohol was investigated for comparison. Treatment of 1-phenyl-2-propyn-1-ol (**4**) with acetone in the presence of the chalcogenolate-bridged diruthenium complex (5 mol %) and NH_4BF_4 (10 mol %) at reflux temperature for 3 h afforded the corresponding alkylated product, 4-phenyl-5-hexyn-2-one (**5**). As a result, only the *syn* alkanethiolate- and alkaneselenolate-bridged diruthenium complexes show a catalytic activity for the propargylation of acetone, while *syn* alkanetellurolate- and *anti* benzenechalcogenolate-bridged diruthenium complexes do not show such catalytic activity (Table 1). Detailed results and discussion are given in the Supporting Information.

Previous results of stoichiometric and catalytic reactions indicate that the propargylic substitution reactions proceeded via allenylidene[9−11] intermediates, where only one of the two Ru atoms works as a reactive site throughout the catalytic reaction.[1a,b,d,3] In fact, we have already found that the allenylidene complexes were

Scheme 5



produced by the reactions of the cationic chalcogenolatebridged diruthenium complexes with propargylic alcohol, and they reacted with nucleophiles to give the corresponding propargylic-substituted products in good yields.[3] In sharp contrast, the formation of the allenylidene complexes was not observed in the reactions of *anti* alkanechalcogenolate-bridged diruthenium complexes with propargylic alcohols such as **4** and 1,1-di-*p*-tolyl-2-propyn-1-ol in the presence of NH_4BF_4 (Scheme 5). Similarly, we have also confirmed no formation of the corresponding allenylidene complexes by the reactions of *anti* benzenechalcogenolate-bridged diruthenium complexes with propargylic alcohol in the presence of NH_4BF_4. These results indicate that the reason the *anti* diruthenium complexes showed no or only low catalytic activity is the difficulty of formation of the allenylidene intermediates in the reactions with propargylic alcohols due to steric repulsion between the Cp* ring of the complex and the substituents of allenylidene ligand, as shown in Scheme 5. As another possibility, the different abilities of the two isomers for dissociation of a chloride ligand in the solvent in the presence of NH_4BF_4 may be considered. The fact that some *anti* alkaneselenolate-bridged diruthenium complexes show a low catalytic activity may indicate some isomerization from *anti* isomer to *syn* isomer during the reaction between *anti* diruthenium complexes and propargylic alcohols.[1d] As to the alkanetellurolate-bridged diruthenium complexes, the difficulty of charge transfer in the tellurolate-bridged diruthenium complexes may correspond to their quite low catalytic activity, as the charge transfer may be considered to be one of the important factors for the catalytic alkylation, one Ru moiety working as an electron pool or a mobile ligand to another Ru moiety.[3,12]

Supporting Information Available: Experimental procedure and crystallographic data of *anti*-**2a**, *anti*-**2b**, *syn*-**3b**, *anti*-**2c**, *syn*-**2d**, *syn*-**2b′**, *syn*-**2d′**, *anti*-**1e**, *anti*-**2e**, and **1e′** and detailed results of the catalytic reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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