Preparation of Dicationic Chalcogenolate-Bridged Diruthenium Complexes and Their Dual Catalytic Activity toward Reactions between Propargylic Alcohols and Acetone

Gen Onodera,† Hideyuki Matsumoto,† Yoshiaki Nishibayashi,*,‡ and Sakae Uemura†

Department of Energy and Hydrocarbon Chemistry, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan, and Institute of Engineering Innovation, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113-8656, Japan

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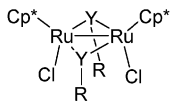
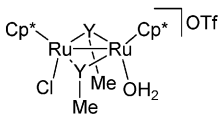
*Summary: Dicationic chalcogenolate-bridged diruthenium complexes have been newly prepared by reactions of the neutral diruthenium dichloride complexes [Cp*RuCl(μ2-YR)]2 (Y = S, Se, Te; R = Me, iPr) with 2 equiv of silver trifluoromethanesulfonate. Reactions of propargylic alcohols with acetone in the presence of a catalytic amount of these dicationic complexes afford the corresponding hexadienones in moderate to good yields, in sharp contrast to the formation of γ-ketoalkynes when neutral or monocationic diruthenium complexes are employed as catalysts.*

We have recently disclosed the novel catalytic activity of thiolate-bridged diruthenium complexes such as $[Cp^*RuCl(\mu_2\text{-}YR)]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$; YR = SMe (met-DIRUX; **1a**), S^{i}Pr (**1b**), SeMe (**1c**), TeMe (**1d**)) and $[Cp^*RuCl(\mu_2\text{-}YMe)_2RuCp^*(OH_2)]OTf$ (OTf = OSO_2CF_3, Y = S (met-DIRUX-OTf; **2a**), Se (**2c**), Te (**2d**)) (Chart 1).[1−3] These complexes were revealed to be suitable catalysts for propargylic substitution reactions of propargylic alcohols with a variety of heteroatom- and carbon-centered nucleophiles to give the corresponding propargylic substituted compounds in high yields with complete regioselectivity.[3] Typically, reactions of propargylic alcohols with acetone in the presence of neutral or monocationic thiolate- and selenolate-bridged diruthenium complexes gave the corresponding propargylic alkylated compounds in high yields without any other compounds (Scheme 1).[2,3b] As an extension of our ongoing study on chalcogenolate-bridged diruthenium complexes, we have now succeeded in preparing dicationic chalcogenolate-bridged diruthenium complexes directly from reactions of neutral diruthenium complexes with 2 equiv of silver trifluoromethanesulfonate (AgOTf). The molecular structure of a dicationic thiolate-bridged diruthenium complex was confirmed by X-ray analysis. Additionally, a novel catalytic activity of these dicationic diruthenium complexes toward reactions of propargylic alcohols with acetone is presented here.

Chart 1

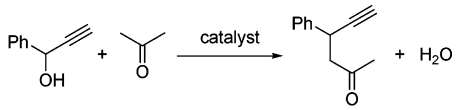


YR = SMe (met-DIRUX; **1a**), S^{i}Pr (**1b**), SeMe (**1c**), TeMe (**1d**)



Y = S (met-DIRUX-OTf; **2a**), Se (**2c**), Te (**2d**)

Scheme 1



catalyst: **1a**, **1b**, **1c**, **2a**, and **2c**.

Treatment of **1a**[2a] and **1b**[2b] with 2 equiv of AgOTf in acetone at room temperature for 24 h gave the corre-

* To whom correspondence should be addressed. E-mail: ynishiba@sogo.t.u-tokyo.ac.jp.
† Kyoto University.
‡ The University of Tokyo.

(1) (a) The thiolate-bridged diruthenium complexes were found to provide a unique bimetallic reaction site 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 complexes are commercially available from Wako Pure Chemical Industries (Japan) as met-DIRUX (*met*hanethiolate-bridged *diru*thenium complex; **1a**, 130-14581) and met-DIRUX-OTf (**2a**, 132-14781).

(2) For the preparation of neutral chalcogenolate-bridged diruthenium complexes and their catalytic activities toward propargylic substitution reactions, see: (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.

(3) (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) Nishibayashi, Y.; Inada, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 7900. (d) Nishibayashi, Y.; Yoshikawa, M.; Inada, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 11846. (e) Inada, Y.; Nishibayashi, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 15172. (f) Nishibayashi, Y.; Onodera, G.; Inada, Y.; Hidai, M.; Uemura, S. *Organometallics* **2003**, *22*, 873. (g) Nishibayashi, Y.; Inada, Y.; Yoshikawa, M.; Hidai, M.; Uemura, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 1495. (h) Nishibayashi, Y.; Yoshikawa, M.; Inada, Y.; Milton, M. D.; Hidai, M.; Uemura, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 2681. (i) Nishibayashi, Y.; Inada, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 7900. (j) Milton, M. D.; Onodera, G.; Nishibayashi, Y.; Uemura, S. *Org. Lett.* **2004**, *6*, 3993. (k) Milton, M. D.; Inada, Y.; Nishibayashi, Y.; Uemura, S. *Chem. Commun.* **2004**, 2712. (l) Nishibayashi, Y.; Yoshikawa, M.; Inada, Y.; D.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2004**, *126*, 16066. (m) Nishibayashi, Y.; Milton, M. D.; Inada, Y.; Yoshikawa, M.; Wakiji, I.; Hidai, M.; Uemura, S. *Chem. Eur. J.* **2005**, *11*, 1433. (n) Ammal, S. C.; Yoshikai, N.; Inada, Y.; Nishibayashi, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2005**, *127*, 9428. (o) Onodera, G.; Matsumoto, H.; Milton, M. D.; Nishibayashi, Y.; Uemura, S. *Org. Lett.* **2005**, *7*, 4029.

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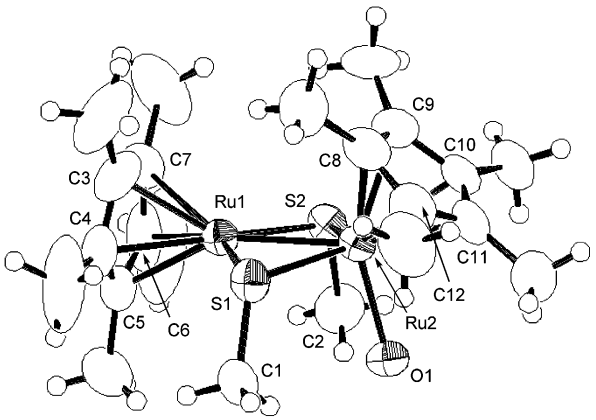
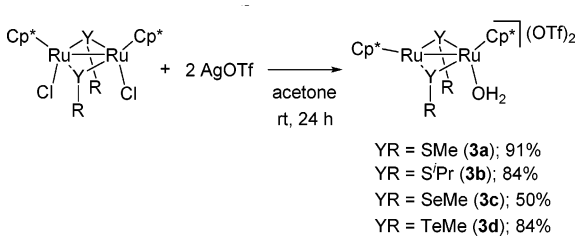


Figure 1. Crystal structure of [Cp*Ru(μ_2-SMe)RuCp*-(OH_2)](OTf)$_2$ (**3a**) with 50% probability ellipsoids. The hydrogen atoms in OH_2 and the OTf anion are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−Ru(2) = 2.612(2), Ru(1)−S(1) = 2.290(5), Ru(1)−S(2) =2.292(5), Ru(2)−S(1) = 2.298(5), Ru(2)−S(2) = 2.297(5), Ru(2)−O(1) = 2.17(1); Ru(1)−Ru(2)−S(1) = 55.2(1), Ru(1)−Ru(2)−S(2) = 55.2(1), Ru(2)−Ru(1)−S(1) = 55.4(1), Ru(2)−Ru(1)−S(2) = 55.4(1), S(1)−Ru(1)−S(2) = 109.7(2), S(1)−Ru(2)−S(2) = 109.3(2), Ru(1)−S(1)−Ru(2) = 69.4(2), Ru(1)−S(2)−Ru(2) = 69.4(1), Ru(1)−Ru(2)−O(1) 101.7(4).

Scheme 2



sponding dicationic thiolate-bridged diruthenium complexes [Cp*Ru(μ_2-SR)$_2$RuCp*(OH_2)](OTf)$_2$ (**3a**, R = Me; **3b**, R = ^{i}Pr) in 91% and 84% isolated yields, respectively (Scheme 2). Similarly, the dicationic selenolate- and tellurolate-bridged diruthenium complexes [Cp*Ru(μ_2-YMe)$_2$RuCp*(OH_2)](OTf)$_2$ (**3c**, Y = Se; **3d**, Y = Te) were prepared in 50% and 84% yields, respectively, from reactions of **1c**[2a] and **1d**[2a] with 2 equiv of AgOTf (Scheme 2). The molecular structure of **3a** was determined by X-ray analysis. An ORTEP drawing of **3a** is shown in Figure 1, which clearly shows that one ruthenium has a vacant site and one of the two Cp* rings lies on a horizontal axis. The bond length of Ru−Ru (2.61 Å) in **3a** is shorter than Ru−Ru bond lengths in **1a** (2.84 Å) and **2a** (2.80 Å).[2a] Selected bond lengths and angles of **3a** are shown in Figure 1.

Next, the catalytic activity of these dicationic diruthenium complexes (**3**) toward reactions of propargylic alcohols with acetone was investigated. Treatment of 1-phenyl-2-propyn-1-ol (**4a**) with acetone in the presence of 5 mol % of **3a** at reflux temperature for 20 h gave (3*E*,5*E*)-6-phenyl-3,5-hexadien-2-one (**5a**) in 32% GLC yield together with cinnamaldehyde (**6a**) (37% GLC yield) (Scheme 3). The stereochemistry of **5a** was determined by ^{1}H NMR.[4] A longer reaction time such

Scheme 3

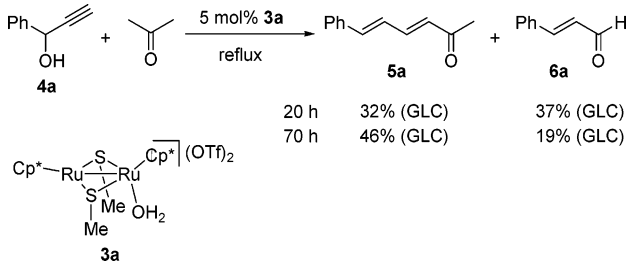
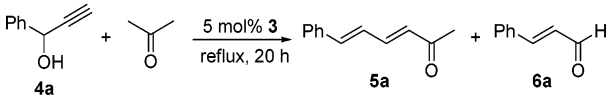


Table 1. Reactions of 4a with Acetone in the Presence of a Catalytic Amount of Various Dicationic Diruthenium Complexes[a]



run	dicationic diruthenium complex (**3**)	yield *(%)*[b] **5a**	**6a**
1	[Cp*Ru(μ_2-SMe)$_2$RuCp*(OH_2)](OTf)$_2$ (**3a**)	32	6
2	[Cp*Ru(μ_2-S^{i}Pr)$_2$RuCp*(OH_2)](OTf)$_2$ (**3b**)	31	7
3	[Cp*Ru(μ_2-SeMe)$_2$RuCp*(OH_2)](OTf)$_2$ (**3c**)	34	11
4	[Cp*Ru(μ_2-TeMe)$_2$RuCp*(OH_2)](OTf)$_2$ (**3d**)	31	24

[a] All reactions of **4a** (0.1 mmol) were carried out in the presence of **3** (0.005 mmol) formed in situ from **1** (0.005 mmol) and AgOTf (0.01 mmol) in acetone (3 mL) at reflux temperature for 20 h. [b] GLC yield.

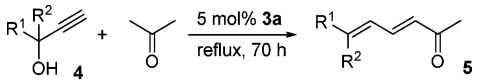
as 70 h increased the yield of **5a** to 46% GLC yield with a decrease of **6a** to 19% GLC yield. The result is in sharp contrast to the formation of 4-phenyl-5-hexyn-2-one when neutral or monocationic thiolate- and selenolate-bridged diruthenium complexes were used as catalysts (Scheme 1).[2,3b] The yield of **5a** was nearly the same in reactions by use of either the in situ formed dicationic diruthenium complex **3a** or the isolated one. Typical results are shown in Table 1.[5] For comparison, catalytic activities of other dicationic diruthenium complexes were investigated in the reaction of **4a** with acetone at reflux temperature for 20 h. Use of dicationic selenolate- and tellurolate-bridged diruthenium complexes (**3c**,**d**) also afforded **5a** in moderate yields (Table 1, runs 3 and 4). It is noteworthy that although the use of a neutral or monocationic tellurolate-bridged diruthenium complex (**1d** or **2d**) did not promote propargylic alkylation of propargylic alcohols with acetone,[2] the dicationic complex (**3d**) showed catalytic activity for the formation of **5a** and **6a**.

Reactions of various propargylic alcohols (**4**) with acetone in the presence of a catalytic amount of **3a** were carried out, typical results being shown in Table 2. Thus, the reaction of propargylic alcohol bearing a 2-naphthyl moiety with acetone gave the corresponding (3*E*,5*E*)-3,5-hexadien-2-one (**5b**) in 42% isolated yield (Table 2, run 2). The introduction of a 4-methyl group at the benzene ring of **4** slightly increased the yield of the product **5c** (Table 2, run 3). In contrast, the introduction of 2-methyl, 4-chloro, or 4-methoxyl moiety decreased the yield of the corresponding dienone **5** (Table 2, runs 4−6). Reactions of 1,1-diaryl-substituted propargylic alcohols with acetone also proceeded to give the corresponding 6,6-diaryl-3,5-hexadien-2-ones (**5g**,**h**) in moderate to good yields (Table 2, runs 7 and 8).

(4) (3*E*,5*E*)-6-Phenylhexa-3,5-diene-2-one (**5a**) was identified by comparing its spectroscopic data with those in the literature; Mitsudo, T.; Takagi, M.; Zhang, S.-W.; Watanabe, Y. *J. Organomet. Chem.* **1992**, *423*, 405.

(5) The formation of some polymers, which might be derived from **4** and products, is one reason for the low yield of both **5** and **6**.

Table 2. Reactions of Various Propargylic Alcohols (4) with Acetone in the Presence of a Catalytic Amount of a Dicationic Methanethiolate-Bridged Diruthenium Complex (3a)[a]



run	propargylic alcohol (4) R1	R2		yield of 5 (%)[b]
1	Ph	H	**4a**	46 (**5a**)
2	2-naphthyl	H	**4b**	42 (**5b**)
3	4-$CH_3C_6H_4$	H	**4c**	54 (**5c**)
4	2-$CH_3C_6H_4$	H	**4d**	39 (**5d**)
5	4-ClC_6H_4	H	**4e**	29 (**5e**)
6	4-$CH_3OC_6H_4$	H	**4f**	15 (**5f**)
7	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	**4g**	28 (**5g**)
8	Ph	Ph	**4h**	53 (**5h**)

[a] All reactions of **4** (0.6 mmol) were carried out in the presence of **3a** (0.03 mmol) in acetone (70 mL) at reflux temperature for 70 h. In all cases, the yield of aldehydes **6** was less than *5%*. [b] Isolated yield.

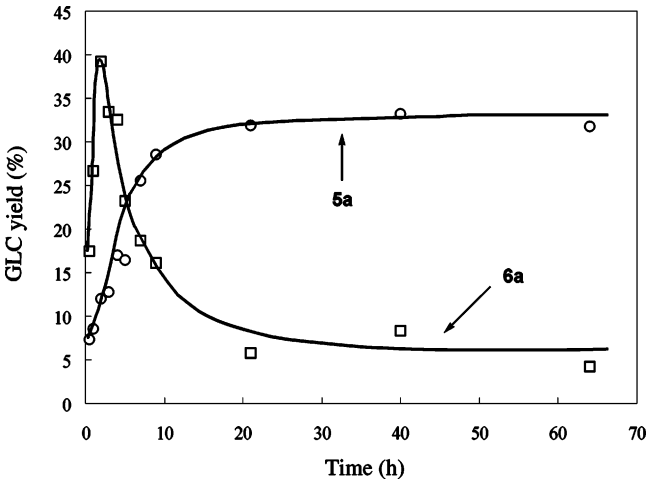
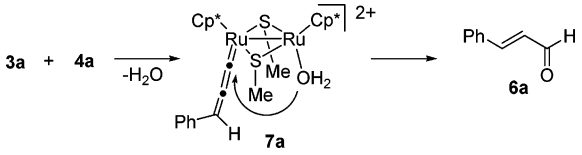


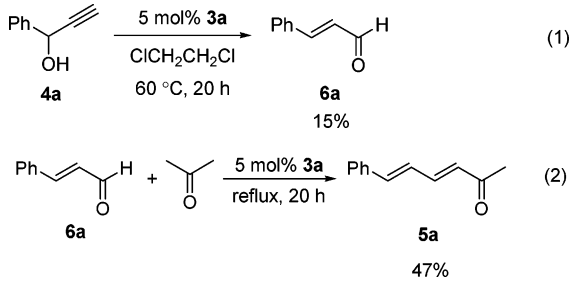
Figure 2. Time profile of the reaction of **4a** with acetone in the presence of a catalytic amount of **3a**.

Scheme 4



The reaction of 1,3-diphenyl-2-propyn-1-ol with acetone under the same reaction conditions gave only 1,3-diphenyl-2-propen-1-one in 59% yield as a mixture of two stereoisomers (*E*/*Z* = 0.7/1.0). This result indicated that only the use of propargylic alcohols bearing a terminal alkyne could afford the corresponding 3,5-hexadien-2-ones.

To obtain some information on the reaction mechanism, we monitored the reaction of **4a** with acetone in the presence of a catalytic amount of **3a** (5 mol %). The time-profile of the reaction is shown in Figure 2, which indicates that the catalytic formation of **5a** proceeded via an initial isomerization of **4a** into cinnamaldehyde (**6a**), followed by aldol condensation between **6a** and acetone and then dehydration. In fact, heating of **4a** in 1,2-dichloroethane ($ClCH_2CH_2Cl$) in the presence of a catalytic amount of **3a** gave only **6a** (eq 1),[6] while the separate reaction of **6a** with acetone in the presence of a catalytic amount of **3a** gave **5a** (eq 2). We consider



that the isomerization from **4a** into **6a** proceeds via an intramolecular nucleophilic attack of coordinated water at an electropositive α-carbon of an intermediate allenylidene ligand (Scheme 4).[7−10] Then, a dicationic diruthenium complex works as a Lewis acid to promote the aldol condensation between **6a** and acetone. Thus, the dual catalytic activity of dicationic chalcogenolate-bridged diruthenium complexes is essential to promote the present novel reaction between propargylic alcohols and acetone.

In summary, we have newly prepared dicationic chalcogenolate-bridged diruthenium complexes by reactions of neutral diruthenium dichloride complexes with 2 equiv of AgOTf. We have found that these dicationic diruthenium complexes catalytically promote novel reactions between propargylic alcohols and acetone to afford the corresponding 3,5-hexadien-2-ones, in sharp contrast to the formation of γ-ketoalkynes when neutral or monocationic diruthenium complexes are employed as catalysts. Further work for elucidation of the detailed reaction mechanism and for broadening the scope of the dual catalytic activity of their dicationic diruthenium complexes is currently in progress.

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Supporting Information Available: Text giving experimental procedures and spectral data for all new compounds a CIF file giving crystallographic data for **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) This type of isomerization reaction is known as the Meyer−Schuster and Rupe rearrangements: (a) Meyer, K. H.; Schuster, K. *Chem. Ber.* **1922**, *55*, 819. (b) Rupe, H.; Kambli, E. *Helv. Chim. Acta* **1926**, *9*, 672. For a review, see: (c) Swaminathan, S.; Narayanan, K. V. *Chem. Rev.* **1971**, *71*, 429 and references therein.

(7) Nucleophilic attack of water at an electrophilic C_α carbon of an allenylidene ligand has been reported: Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423.

(8) The ruthenium-catalyzed isomerization of propargylic alcohols into the corresponding α,β-unsaturaed aldehydes was reported: Cadirno, V.; Díez, J.; García-Garrido, S. E.; Gimeno, J. *Chem. Commun.* **2004**, 2716.

(9) Wakatsuki and co-workers proposed that allenylidene complexes were reactive intermediates in the isomerization of propargylic alcohols into the corresponding α,β-unsaturated aldehydes catalyzed by some ruthenium complexes: Suzuki, T.; Tokunaga, M.; Wakatsuki, Y. *Tetrahedron Lett.* **2002**, *43*, 7531.

(10) As described in our previous papers,[2,3] the intermolecular attack of various nucleophiles such as alcohols occurs selectively at the C_γ atom of the allenylidene ligand on dinuclear ruthenium complexes to give the corresponding propargylic substituted products such as propargylic ethers in high yields with complete selectivity.