Conversion of Allylic Alcohols to Carbonyl Compounds Catalyzed by Alkoxy-Bridged Dinuclear Areneruthenium Complexes

Yasutomo Takai, Ryo Kitaura, Emi Nakatani, Takafumi Onishi, and Hideo Kurosawa*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565-0871, Japan

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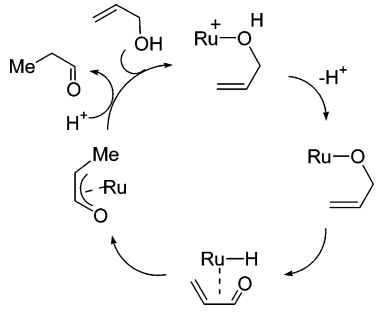
Visible light irradiation of an azobenzene-bridged dinuclear ruthenium complex ligated by a η^6-arene group having a pendant alkoxy ligand, $[Ru_2\{\eta^6{:}\eta^1{:}\mu\text{-}C_6H_5(CH_2)_3O\}_2(\mu\text{-}C_6H_5N{=}NC_6H_4OMe)]BF_4$, led to generation of an active species capable of catalyzing isomerization of allyl alcohols to the corresponding carbonyl compounds under mild conditions. Treatment of the chloro-bridged dinuclear complex $[Ru_2\{\eta^6{:}\eta^1{:}\mu\text{-}C_6H_5(CH_2)_3O\}_2(\mu\text{-Cl})]BF_4$ with 1 equiv AgOTf or that of the methoxy-bridged complex $[Ru_2\{\eta^6{:}\eta^1{:}\mu\text{-}C_6H_5(CH_2)_3O\}_2(\mu\text{-OMe})]BF_4$ with HOTf also resulted in generation of catalyst for the isomerization, while these dinuclear complexes themselves were inactive as the isomerization catalyst. Reaction of the hydride-bridged dinuclear complex $[Ru_2\{\eta^6{:}\eta^1{:}\mu\text{-}C_6H_5(CH_2)_3O\}_2(\mu\text{-H})]BF_4$ with methyl vinyl ketone gave the allyloxy-bridged dinuclear complex $[Ru_2\{\eta^6{:}\eta^1{:}\mu\text{-}C_6H_5(CH_2)_3O\}_2(\mu\text{-OCHMeCH}{=}CH_2)]BF_4$ rather sluggishly, while the same reactants in the presence of an equimolar amount of HOTf rapidly gave $CH_3COCH_2CH_3$ and the triflate complex $[Ru_2\{\eta^6{:}\eta^1{:}\mu\text{-}C_6H_5(CH_2)_3O\}_2(\mu\text{-OTf})]BF_4$. A mechanistic scheme for the isomerization of allyl alcohols involving the dinuclear acceptor $[Ru_2\{\eta^6{:}\eta^1{:}\mu\text{-}C_6H_5(CH_2)_3O\}_2]^{2+}$ as a key species has been discussed.

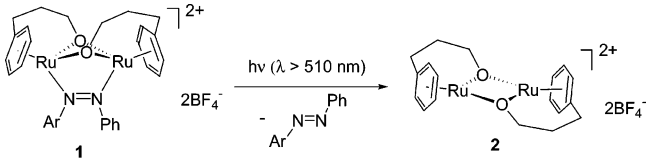
Introduction

Increasing attention has been paid to isomerization of allylic alcohols to carbonyl compounds catalyzed by complexes of some transition metals[1] including ruthenium.[2] The ruthenium complexes used as catalyst precursor contained a few kinds of organic ligands such as polyene, cyclopentadienyl, indenyl, and arene. Most of the successful catalyst systems have been thought to proceed through initial binding of the alcoholic oxygen to a coordinatively unsaturated ruthenium center, mostly of the cationic type, followed by deprotonation to give a metal allyloxide intermediate and hydrogen shift via Ru−H bond formation and cleavage (Scheme 1).[3] In our previous studies on areneruthenium complexes containing pendant alkoxy ligands,[4] we reported that photoirradiation of a dinuclear areneruthenium complex having a *cis*-azobenzene bridge (**1**) resulted in release of *trans*-azobenzene and generation of a coordinatively unsaturated dinuclear unit (**2**) (Scheme 2).[4b] We then examined the activity of this unsaturated dinuclear unit in catalyzing the isomerization of allylic

Scheme 1



Scheme 2[a]



[a] Ar = p-$MeOC_6H_4$.

(1) Van Drift, R. C.; Bouwman, E.; Drent, E. *J. Organomet. Chem*. **2002**, *650*, 1.

(2) (a)Trost, B. M.; Kulawiec, R. J. *J. Am. Chem. Soc*. **1993**, *115*, 2027. (b) Backvall, J. E.; Andreasson, U. *Tetrahedron Lett*. **1993**, *34*, 5459. (c) McGrath, D. V.; Grubbs, R. H. *Organometallics* **1994**, *13*, 224. (d) Slugovc, C.; Ruba, E.; Schmid, R.; Kirchner, K. *Organometallics* **1999**, *18*, 4230. (e) Van der Drift, R. C.; Vailati, M.; Bouwman, E.; Drent, E. *J. Mol. Catal. A, Chem*. **2000**, *159*, 163. (f) Van der Drift, R. C.; Bouwman, E.; Drent, E.; Kooijman, H.; Spek, A. L.; Van Oort, A. B.; Mul, W. P. *Organometallics* **2002**, *21*, 3401. (g) Van der Drift, R. C.; Sprengers, J. W.; Bouwman, E.; Mul, W. R.; Kooijman, H.; Spek, A. L.; Drent, E. *Eur. J. Inorg. Chem*. **2002**, 2147. (h) Cadierao, V.; Garcia-Garrido, S. E.; Gimeno, J. *Chem. Commun*. **2004**, 232. (i) Van der Drift, R. C.; Gagliardo, M.; Kooijman, H.; Spek, A. L.; Bouwman, E.; Drent, E. *J. Organomet. Chem*. **2005**, *690*, 1044. (j) Ito, M.; Kitahara, S.; Ikariya, T. *J. Am. Chem. Soc*. **2005**, *127*, 6172.

(3) (a) The initial binding of allyl alcohol by metal via η^2-olefin coordination is involved in the original proposal,[2a] although without any direct proof. (b) A possibility of hydrogen transfer without β-elimination of the metal allyloxide intermediate has been offered.[2j]

(4) (a) Miyaki, Y.; Onishi, T.; Kurosawa, H. *Inorg. Chim. Acta* **2000**, *300−302*, 369. (b) Kitaura, R.; Miyaki, Y.; Onishi, T.; Kurosawa, H. *Inorg. Chim. Acta* **2002**, *334*, 142.

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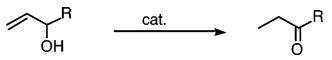
Table 1. Catalytic Isomerization of Allylic Alcohol[a]



R	time (h)	yield (%)
H	16	83[b]
Me	5	74
Et	5	86

[a] Conditions: [substrate] = 0.4 mmol, [cat.] = 0.01 mmol, in CD_2Cl_2 (0.6 mL) at room temperature. Cat. was generated by irradiation of **1** with a tungsten lamp for 5 min. [b] 8% of diallyl ether formed.

alcohols to give carbonyl compounds under very mild conditions. Moreover, further mechanistic insights into the catalysis were gained through some key experiments focusing on stoichiometric reactions and variable-temperature NMR studies on intermediate model complexes including dinuclear complexes having bridging hydrido ligands and alcoholic ligands.

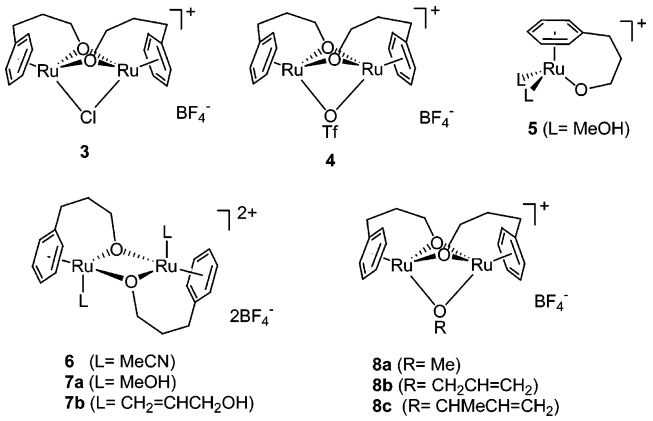
Results and Discussion

When we irradiated a CD_2C1_2 solution (0.6 mL) containing **1** (0.01 mmol) and allyl alcohol (0.4 mmol) with a tungsten lamp (O-54 filter; $\lambda > 510$ nm) at 25 °C for 5 min, isomerization of allyl alcohol to propionaldehyde commenced immediately. The reaction was monitored by ^{1}H NMR measurements, with the yield of propionaldehyde reaching 83% after 16 h (Table 1). It should be noted that allyl alcohol remained unchanged when the initial irradiation was skipped and the mixture kept in the dark. Similarly to the phototriggered isomerization of allyl alcohol, l-buten-3-ol and l-penten-3-ol underwent isomerization to give the corresponding ketones in 74% and 86% yields, respectively, after 5 h (Table 1). The very mild conditions employed in this study (25 °C) may be contrasted to the conditions (57 °C or higher) in other Ru complex-catalyzed isomerizations of allylic alcohols[2] except for some unusually efficient catalysis systems.[2c,j] It was also reported that generation of enols and carbonyl compounds from allylic alcohols takes place rapidly at 25 °C by the use of cationic Rh complexes.[5] It was found, however, that the photoirradiation of **1** is not effective in catalyzing isomerization of cinnamyl alcohol and cyclohexen-3-ol at room temperature.

Like the coordinatively saturated complex **1**, another saturated complex, $[Ru_2\{\eta^6{:}\eta^1{:}\mu\text{-}C_6H_5(CH_2)_3O\}_2(\mu\text{-}Cl)]BF_4$ (**3**)[4b] (Scheme 3), was totally inactive for the isomerization of the allyl alcohol. When **3** was treated with 1 equiv of AgOTf in CD_2Cl_2 in the presence of allyl alcohol, the formation of propionaldehyde (ca. 60%) was confirmed after 16 h. From the reaction of **3** with AgOTf without allyl alcohol, the triflate complex $[Ru_2\{\eta^6{:}\eta^1{:}\mu\text{-}C_6H_5(CH_2)_3O\}_2(OTf)]BF_4$ (**4**) was obtained as an isolable, though highly unstable, solid. This solid was found indeed to catalyze isomerization of allyl alcohol to propionaldehyde in a rate comparable to that of the reaction carried out by the use of **3** and AgOTf.

For the mechanism of Ru-catalyzed isomerization of allyl alcohol it has been proposed that the catalytic cycle starts from coordination to ruthenium of the oxygen of the alcohol, which becomes an allyloxide ligand by deprotonation (see Scheme 1). The allyloxide would then undergo β-hydrogen elimination to give ruthenium hydride and an α,β-enal or enone ligand. Finally the hydride and enal (or enone) rearrange to an enolate complex (either O-bound, C-bound, or η^3-bound), which may undergo protonolysis to furnish the carbonyl product and regenerate the coordinatively unsaturated ruthenium center. We attempted some experiments to substantiate the catalytic cycle represented by Scheme 1.

Scheme 3



It was found that the catalyst system derived from irradiation of **1** is not active in isomerization of allylbenzene to β-methylstyrene. This is consistent with, but not necessarily indicative of, the path of Scheme 1 involving coordination of alcoholic oxygen and the subsequent β-H elimination of the allyloxy intermediate. Then we wanted to know in what type of structure the catalytically active ruthenium moiety accommodates the alcoholic substrate. For this purpose a ^{1}H NMR examination was made on a model solution obtained by irradiating a solution of **1** (0.01 mmol) in a mixture of CD_3OD (0.3 mL) and CD_2C1_2 (0.3 mL) for 5 min. The spectrum of this solution at room temperature exhibited, in addition to the resonances due to free *trans*-azobenzene, three broad peaks due to ortho- (δ 4.94), meta- (δ 5.48), and para-hydrogens (δ 5.19) of the arene ring and three broad signals (δ 4.09, 2.26, 2.43) due to the sidearm group of $OCH_2CH_2CH_2Ph$. At lower temperatures (−60 °C or lower) the ortho-hydrogen resonance split into two broad peaks (δ 4.85, 4.92), while the meta-hydrogen resonance remained nonsplit. With regard to the sidearm proton resonances of the $OCH_2CH_2CH_2Ph$ ligand, the OCH_2 and CH_2Ph signals each split into two peaks (δ 3.82, 4.17 and δ 2.2, 2.54), this being consistent with inequivalency of the two hydrogens in each CH_2 group, although the third CH_2 resonance (δ 2.26) appeared as one broad peak.

These splitting patterns of the $\eta^6{:}\eta^1$-$C_6H_5CH_2CH_2CH_2O$ ligand at the lower temperature strongly suggest that a structure of the primary species in the model solution cannot contain a mirror plane passing through the ipso and para carbons of the η^6-C_6H_5 group, as represented by, for example, a monomeric species **5** (Scheme 3). Rather, the splitting patterns are more consistent with a structure of the intermediate having a C_2 or S_2 symmetry, arising from dimerization of the $(\eta^6{:}\eta^1$-$C_6H_5CH_2CH_2CH_2O)Ru$ unit, as represented by **3**,

(5) Bergens, S. H.; Bosnich, B. *J. Am. Chem. Soc.* **1991**, *113*, 958.

or the acetonitrile-coordinated dimer **6** (Scheme 3), respectively. Indeed, it was already reported[4b] that the complex **6** shows a quite similar variable-temperature ^{1}H NMR pattern attributable to a time-averaged symmetric structure having a mirror plane at room temperature and a frozen structure having an inversion center at −40 °C. Thus, we believe that the complex **7a** (L = MeOH) is the primary species existing in the model solution. Then in the catalytic reaction also, two allyl alcohol molecules would coordinate to the unsaturated dimeric unit through the hydroxy oxygen to form **7b** (L = CH_2=$CHCH_2OH$) without initial coordination of the C=C bond; no spectral evidence for this type of coordination has been obtained in the mixture of allylbenzene and **1** after irradiation.

Variable-temperature ^{1}H NMR spectra of the triflate complex **4** suggest that the complex contains a weakly bridging triflate ligand, which undergoes ionic dissociation to cause fluxional coordination behavior. Although somewhat unstable at room temperature, the complex showed proton resonances at −20 to −60 °C rather simple for a chiral dinuclear structure; there appeared three sets of resonances for the aryl protons and also three sets for the sidearm group protons of the C_6H_5-$CH_2CH_2CH_2O$ ligand (see Experimental Section), consistent with the presence of a time-averaged mirror plane in the molecule. On lowering the temperature below −70 °C, some of the resonances (ortho aryl protons, $CH_2CH_2CH_2O$ and CH_2O protons, each integrating 4H) began to broaden and became split into two broad resonances, respectively (Experimental Section). These lower temperature spectral features are consistent with the molecule having a C_2 symmetry with the bridging triflate ligand. The time-averaged mirror symmetry at the higher temperature most probably is caused by rapid dissociation of the triflate anion from **4**, followed by its reassociation with **2** from both sides of a pseudosquare plane of $[RuORuO]^{2+}$. It is also interesting to note that addition of 10 equiv of MeCN to **4** in CD_2Cl_2 resulted in immediate formation of acetonitrile-coordinated complex **6** (counteranion, OTf^- and BF_4^-).

Next we took interest in the preparation and catalytic activity of methoxy-bridged dinuclear complex **8a**, as we thought that **8a** and allyl alcohol would readily afford an allyloxide ruthenium complex that may play a key role in the catalytic cycle (see Scheme 1). The complex **8a** was prepared in a manner similar to that for the structurally related, simpler analogue $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OMe)_3]BPh_4$.[6] The molecular structure of **8a** (Figure 1) is similar to that of the latter dimeric complex.[6b] It should be noted, however, that **8a** was totally inactive by itself with regard to isomerization of allyl alcohol. ^{1}H NMR measurements on a mixture of **8a** and CH_2=$CHCH_2OH$ suggested formation of allyloxy-bridged dinuclear complex **8b** (see Experimental Section), although isolation of a pure sample of **8b** failed. Remarkably, the catalytic isomerization of CH_2=$CHCH_2OH$ was attained when HOTf was added to **8a** as long as the ratio HOTf/**8a** was adjusted to 1/1 (72% of propionaldehyde after 16 h). ^{1}H NMR spectra of a mixture of **8a** and 1 equiv of HOTf showed resonances similar to those of the isolated triflate complex **4**. On the other hand, addition of more than 1 equiv of HOTf to **8a** resulted in the lower activity for the formation of propionaldehyde, with the yield of diallyl ether having increased; for example, treatment of CH_2=$CHCH_2OH$ (0.4 mmol) with **8a** (0.01 mmol) and HOTf (0.03 mmol) in CH_2Cl_2 (0.6 mL) at room temperature for 24 h (60% conversion) afforded a much higher yield of diallyl ether (50%) than propionaldehyde (7%).[7] ^{1}H NMR spectra of a CD_2Cl_2 solution of a mixture of **8a** and HOTf (1:3) showed a set of resonances that are different from those of **4** (see Experimental Section), but no definitive structure estimation can be made with regard to the primary species in the 3:1 mixture of HOTf and **8a** except that η^6-arene coordination is maintained. At any rate, it is notable that the change of the molar ratio of HOTf/**8a** can affect the course of the reaction of allyl alcohol. Somewhat related to this, Bouwman and co-workers reported that some $[CpRu(diphos)]^+$ systems catalyzed the conversion of allyl alcohols, with the isoprene addend playing the role of an "on-off switch" between isomerization and allyl ether formation.[2e]

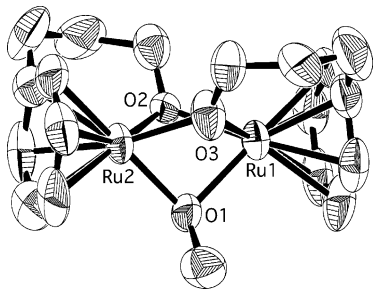


Figure 1. ORTEP drawing of **8a**. BF_4 was omitted for clarity. Selected bond lengths (Å): Ru1−O1 = 2.080(8), Ru1−O2 = 2.054(9), Ru1−O3 = 2.04(1), Ru2−O1 = 2.085(10), Ru2−O2 = 2.025(8), Ru2−O3 = 2.036(9). Selected bond angles (deg): O1−Ru1−O2 = 70.9(3), O1−Ru1−O3 = 72.6(4), O2−Ru1−O3 = 74.7(4), O1−Ru2−O2 = 71.3(4), O1−Ru2−O3 = 72.5(4), O2−Ru2−O3 = 75.3(4), Ru1−O1−Ru2 = 91.5(4), Ru1−O2−Ru2 = 94.0(4), Ru1−O3−Ru2 = 94.2(4).

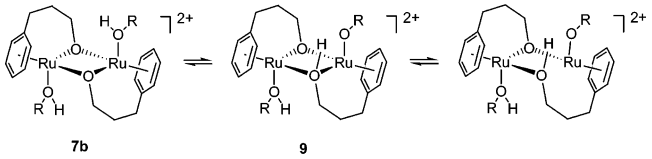
For the β-hydrogen elimination of metal alkoxide to occur, a transition metal center has to be coordinatively unsaturated in general. In the reaction using a trialkoxy dinuclear complex (**8a**) without any H^+ added, it is assumed that the primary species existent in the reaction mixture takes the form $[(\eta^6\text{-arene})Ru(\mu\text{-}OR)_2(\mu\text{-}OCH_2CH$=$CH_2)Ru(\eta^6\text{-arene})]^+$ (R = $CH_2CH_2CH_2Ph$). The reason for the catalytic inactivity of the system involving such a trialkoxy-bridged complex would be that the three alkoxy bridges appear to bond to two ruthenium atoms so tightly that a vacant coordination site necessary for the β-hydrogen elimination cannot readily be provided. Indeed ^{1}H NMR of **8a** in CD_3OD at room temperature showed resonances due to the $C_6H_5CH_2CH_2CH_2O$ ligand consistent with a rigid structure having C_2 symmetry.

In the reaction system involving **7b** derived from allyl alcohol and **2** or a mixture of **8a** and 1 equiv of HOTf, transfer of hydrogen from OH of the coordinating allyl

(6) (a) Arthur, T.; Robertson, D. R.; Tocher, D. A.; Stephenson, T. A. *J. Organomet. Chem.* **1981**, *208*, 389. (b) Gould, R. O.; Stephenson, T. A.; Tocher, D. A. *J. Organomet. Chem.* **1984**, *263*, 375.

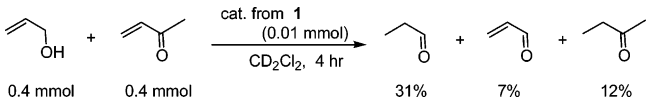
(7) A reference reaction between allyl alcohol and HOTf without employing complex **8a** under otherwise identical conditions showed that HOTf did not catalyze diallyl ether formation.

Scheme 4[a]



[a] R = $CH_2CH{=}CH_2$.

Scheme 5



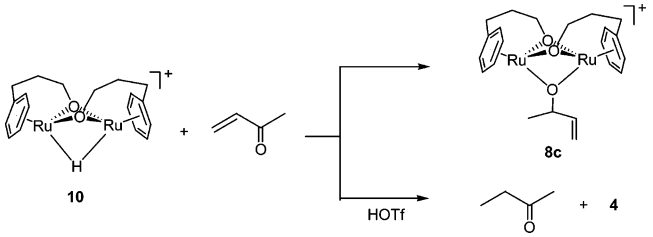
alcohol to the co-ligating sidearm alkoxy-oxygen may give rise to an allyloxo ligand and the new alcohol ligand $-CH_2CH_2CH_2OH$ as in **9** of Scheme 4. Then **9** may readily vacate the coordination site, making one of the ruthenium atoms coordinatively unsaturated (Scheme 4). This may be followed by elimination of the β-hydrogen of the allyloxy ligand. If the concentration of H^+ increases as in the system involving **8a** and more than 1 equiv of HOTf, the concentration of the key unit, i.e., allyloxy ligand, may decrease proportionally.

At the moment we cannot offer any mechanism for the selective formation of diallyl ether in the reaction using a 3:1 ratio of HOTf/**8a**. Bouwman and co-workers proposed the intermediacy of the Ru(IV) allyl complex during [CpRu(diphosphine)]$^+$-catalyzed diallyl ether formation.[2e] A somewhat similar η^3-allyl intermediate was suggested to be responsible for the allyl alkyl ether formation catalyzed by a combination of $[CpRu(MeCN)_3]^+$ and quinolinecarboxylate auxiliary.[8] In our case, however, it seems rather unlikely that a highly electrophilic [(η^6-arene)Ru]$^{2+}$ species, presumed to be formed in the initial stage of the reaction of 3 equiv of H^+ with **8a**, undergoes oxidative addition of allylic alcohol. Rather, coordination of a hydroxy oxygen of an allyl alcohol to an electron-deficient metal center in [(η^6-arene)Ru]$^{2+}$ may enhance susceptibility of the allyl carbon of the coordinated allyl alcohol toward the nucleophilic attack by oxygen of another alcohol. More detailed studies are required before any conclusive suggestions can be made.

Next we gained further insights into the intermediacy of the hydride-enal (enone) complex shown in Scheme 1. Thus, when methyl vinyl ketone (MVK) (0.4 mmol) had been added to a mixture of $CH_2{=}CHCH_2OH$ (0.4 mmol) and **1** (0.01 mmol) prior to visible light irradiation and the reaction was stopped after 4 h, the yield of propionaldehyde decreased to 31% (47% if MVK was not added), and 12% of butan-2-one and 7% of acrolein were formed[9] (Scheme 5). This result strongly suggests exchange of an acrolein ligand on the coordination sphere with external MVK in the stage of the hydride intermediate.

In another examination we prepared a μ-hydride complex[10] (**10**) from **4** and Bu_3SnH and treated **10** with MVK to find an interesting change of the reaction course depending on whether additional H^+ is present in the reagent mixture (Scheme 6). Thus, on one hand the reaction between **10** and MVK proceeded only very sluggishly to give allyloxy-bridged dimer complex **8c**, a product of 1,2-addition of the Ru−H bond to MVK. The complex **8c** remained inert with respect to isomerization to the enolate complex. On the other hand, **10** reacted very rapidly with MVK in the presence of 1 equiv of HOTf to give butan-2-one and triflate-bridged complex **4**, although an enolate intermediate was not detected. The exact role of additional H^+ in changing the reaction course of Ru−H with an α,β-unsaturated carbonyl compound is not clear at the moment. However, it should be stressed here that addition of H^+ to a mixture of **10** and MVK would lead to a species of which the composition is very close to that of a species obtained by β-hydrogen elimination of the allyloxide ligand in the intermediate **9** shown in Scheme 4 except for the additional alcohol ligand.

Scheme 6



Experiments using the deuteride analogue [$Ru_2\{\eta^6{:}\eta^1$-$C_6H_5(CH_2)_3O\}_2(\mu$-D)]$^+$ (**10**-*d*; isotope purity >90%) gave further support for Scheme 1. Thus, reaction of **10**-*d* with MVK (0.5 equiv) and HOTf (1 equiv) in CD_2Cl_2 afforded butan-2-one of which ^{1}H NMR spectra indicated 88% deuterium incorporation at the terminal methyl (position 4), consistent with the attack of the hydride at the vinyl terminal.

Conclusion

Several methods were designed to generate a coordinatively unsaturated alkoxy-bridged dinuclear areneruthenium unit, which was found to effectively induce isomerization of allylic alcohols to carbonyl compounds. The unique structure aspect of the initial stage intermediate for the isomerization formed from such an unsaturated dimeric unit and alcoholic substrate has been assessed. Also, further insights into the intermediacy of the hydride-enal (enone) complex were gained. Further studies are under way in our group directed toward application of the present system to other substrates and more detailed elucidation of stoichiometric steps constructing the catalytic cycle.

Experimental Section

General remarks on the instruments and experimental conditions for treating chemicals and solvents are similar to those already described in the previous series of papers.[4] Preparation of complexes **1** and **3** has been described previously.[4b]

(8) Saburi, H.; Tanaka, S.; Kitamura, M. *Angew. Chem., Int. Ed.* **2005**, *44,* 1730.

(9) The reason for the somewhat lower yield of acrolein than butan-2-one is not clear at the moment. It may well be that acrolein has undergone an as yet unidentified decomposition path rather readily.

(10) The ^{1}H NMR shift for μ-H in **10** (δ −7.95) is comparable to those of the reported diruthenium μ-hydride complexes.[11]

(11) (a) Suss-Fink, G.; Fidalgo, E. G.; Neels, A.; Stoeckli-Evans, H. *J. Organomet. Chem.* **2000**, *602,* 188. (b) Takemoto, S.; Kuwata, S.; Nishibayashi, Y.; Hidai, M. *Organometallics* **2000**, *19*, 3249. (c) Bennett, M. A.; Ennett, J. P. *Organometallics* **1984**, *3*, 1365.

Preparation of $[Ru_2\{\eta^6:\eta^1:\mu\text{-}C_6H_5(CH_2)_3O\}_2(OSO_2CF_3)](BF_4)$ (4). To a solution of **3** (240 mg, 0.4 mmol) in CH_2Cl_2(20 mL) was added AgOTf (105 mg, 0.4 mmol). After stirring for 6 h at room temperature, the mixture was filtered and the solvent was evaporated. The residue was recrystallized from CH_2ClCH_2Cl and Et_2O to give 252 mg (89%) of crystalline product. ^{1}H NMR (CD_2Cl_2, −20 °C): δ 2.26 (m, 4H), 2.51 (t, J = 5.7 Hz, 4H), 4.45 (t, J = 4.3 Hz, 4H), 5.3−5.4 (m, 6H), 5.72 (t, J = 5.9 Hz, 4H). ^{1}H NMR (CD_2Cl_2, −100 °C): δ 1.91 (br, 2H), 2.30 (br, 2H), 2.47 (br m, 4H), 4.34 (br, 2H), 4.58 (br, 2H), 4.97 (br s, 2H), 5.33 (br s, 2H), 5.56 (br, 2H), 5.89 (br, 4H). Anal. Calcd for $C_{19}H_{22}O_5S_1Ru_2BF_7$: C, 32.22; H, 3.13. Found: C, 32.11; H, 3.16. When HOTf (0.02 mmol) was added to a CD_2Cl_2 solution of **4** (0.01 mmol), the ^{1}H NMR spectrum showed the disappearance of peaks due to **4** and new resonances appeared at δ 2.50 (br, 4H), 2.69 (m, 4H), 4.14 (m, 4H), 5.66 (d, J = 6.2 Hz, 4H), 5.98 (t, J = 5.9 Hz, 2H), and 6.36 (t, J = 5.9 Hz, 4H).

Preparation of $[Ru_2\{\eta^6:\eta^1:\mu\text{-}C_6H_5(CH_2)_3O\}_2(\mu\text{-}OMe)](BF_4)$ (8a). To a suspension of $Ru\{\eta^6\text{-}C_6H_5(CH_2)_3OH\}Cl_2$[4a] (200 mg; 0.32 mmol) in MeCN (15 mL) was added a solution of NaOH (52 mg; 1.30 mmol) and $NaBF_4$ (72 mg; 0.66 mmol) in MeOH (5 mL). After being stirred for 12 h at room temperature, the mixture was filtered and the solvents were evaporated under vacuum. The residue was dissolved in CH_2Cl_2, and the suspension was filtered. The filtrate was evaporated, and the residue was recrystallized from MeCN and Et_2O to give 128 mg (67%) of yellow crystals. ^{1}H NMR (CD_3CN): δ 2.27 (m, 4H), 2.37 (m, 2H), 2.58 (m, 2H), 4.00 (m, 2H), 4.22 (m, 2H), 4.29 (s, 3H), 4.97 (d, J = 5.9 Hz, 2H), 5.00 (d, J = 5.5 Hz, 2H), 5.21 (t, J = 5.7 Hz, 2H), 5.50 (t, J = 6.6 Hz, 2H), 5.53 (t, J = 6.4 Hz, 2H). Anal. Calcd for $C_{19}H_{25}O_3BF_4Ru_2$: C, 38.66; H, 4.27. Found: C, 38.73; H, 4.27. Crystal data for **8a**: $C_{19}H_{25}O_3BF_4Ru_2$, M = 590.35, monoclinic, space group $P2_1/c$ (#14), a = 9.7662(8) Å, b = 13.470(1) Å, c = 15.950(2) Å, β = 101.026(3)°, V = 2059.5(3) Å^3, Z = 4, $F(000)$ = 1168, D_c = 1.90 g/cm^3, μ(Mo Kα) = 15.20 cm^{-1}, 262 variables refined with 2730 reflections with $I > 3\sigma(I)$ to R = 0.079, R_w = 0.087.

Preparation of $[Ru_2\{\eta^6:\eta^1:\mu\text{-}C_6H_5(CH_2)_3O\}_2(\mu\text{-}H)](BF_4)$ (10). To a suspension of **3** (600 mg; 1.0 mmol) in 50 mL of CH_2Cl_2 was added 2.5 mL of Bu_3SnH (8.50 mmol). After being stirred for 1 h at room temperature, the solution changed from yellow to red, and the mixture was filtered. The filtrate was evaporated under vacuum, and the residue was recrystallized from CH_2Cl_2 and n-hexane to give 504 mg (90%) of red crystalline products. ^{1}H NMR (CD_2Cl_2): δ −7.95 (s, 1H), 1.7−1.9 (m, 6H), 2.50 (m, 2H), 2.68 (dt, J = 14, 3.5 Hz, 2H), 3.7−3.8 (m, 2H), 4.83 (t, J = 5.7 Hz, 2H), 5.12 (d, J = 5.1 Hz, 2H), 5.70 (d, J = 6.5 Hz, 2H), 5.92 (t, J = 5.9 Hz, 2H), 6.32 (t, J = 5.7 Hz, 2H). Anal. Calcd for $C_{18}H_{25}O_2BF_4Ru_2$: C, 38.58; H, 4.14. Found: C, 38.32; H, 4.17.

General Procedure for Isomerization of Allyl Alcohols Catalyzed by 1. In a typical reaction, to a solution of **1** (8.8 mg; 0.01 mmol) in CD_2Cl_2 (0.6 mL) in an NMR tube was added CH_2═$CHCH_2OH$ (27 μL; 0.4 mmol). On irradiation of the solution with a tungesten lamp using an O-54 filter (λ > 510 nm) for 5 min, the solution turned from purple to orange. The sample tube was left to stand at room temperature, and the reaction was monitored by ^{1}H NMR measurements.

General Procedure for Isomerization of Allyl Alcohol Catalyzed by 8a and HOTf. In a typical reaction, to a solution of **8a** (6 mg; 0.01 mmol) in CD_2Cl_2 (0.6 mL) in an NMR tube was added CH_2═$CHCH_2OH$ (0.4 mmol) and HOTf (0.9 μL; 0.01 mmol). The sample tube was left to stand at room temperature, and the reaction was monitored by ^{1}H NMR measurements.

Reaction of 10 with MVK. To an NMR tube containing a CD_2Cl_2 solution (0.5 mL) of **10** (11 mg; 0.02 mmol) was added 3.3 μL of MVK (0.04 mmol), and the solution was kept at room temperature. ^{1}H NMR measurements after 116 h indicated the presence of **10** (ca. 20%) and formation of new species (80%), presumed to be the μ-allyloxide dinuclear complex $[Ru_2\{\eta^6:\eta^1:\mu\text{-}C_6H_5(CH_2)_3O\}_2(\mu\text{-}OCHMeCH{=}CH_2)](BF_4)$ (**8c**) by comparison of ^{1}H NMR data with those of a crude sample generated by treatment of **8a** with excess 1-buten-3-ol in CH_2Cl_2. A particularly diagnostic ^{1}H NMR feature of **8c** is the appearance of two methyl doublets at δ 1.44 (J = 6.3 Hz) and 1.45 (J = 6.3 Hz) due to CMe α to oxygen, indicating the presence of a diastereomeric pair. Other ^{1}H NMR features of **8c** include: δ 2.36 (m, 6H), 2.65 (m, 2H), 3.95 (m, 2H), 4.30 (m, 2H), 4.9−5.5 (m, 13H), 6.20 (m, 1H). The olefinic (═CH_2) and OCH− proton resonances may have been hidden by aromatic proton resonances at δ 4.9−5.5. Treatment of the reaction mixture from **10** and MVK shown above with 0.05 mL of CD_3OD led to formation of **8a** and free 1-buten-3-ol. Likewise complex **8b** was formed from **8a** and CH_2═$CHCH_2OH$. ^{1}H NMR (CD_2Cl_2): δ 2.3−2.4 (br, 6H), 2.55−2.7 (m, 2H), 4.0 (br m, 2H), 4.3 (br d, 2H), 4.90 (d, J = 5.7 Hz, 4H), 4.98 (d, J = 5.4 Hz, 2H), 5.18 (t, J = 5.4 Hz, 2H), 5.25−5.50 (m, 4H), 6.21 (m, 1H).

Reaction of 10 with MVK in the Presence of HOTf. To a CD_2Cl_2 solution (0.5 mL) of **10** (0.02 mmol) was added MVK (0.04 mmol) and HOTf (1.8 μL; 0.02 mmol). ^{1}H NMR measurements immediately after mixing the reactants indicated quantitative formation of butan-2-one and complex **4**.

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Supporting Information Available: X-ray crystallographic information (CIF) for **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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