## Skeletal Reorganization of Enynes Catalyzed by a Ru(II)–Ru(III) Mixed-valence Complex under an Atmosphere of O<sub>2</sub> or CO

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A mixed-valence Ru(II)–Ru(III) complex was used to catalyze the skeletal reorganization of 1,6-enynes, leading to the production of 1-vinylcyclopentene derivatives. The reaction proceeded optimally in an atmosphere of  $O_2$  or CO. The presence of an alkyl group at the internal olefinic carbon in the starting enyne resulted in an increase in product yield compared to that bearing no substituent on the olefin moiety.

The catalytic cycloisomerization of enynes has recently attracted considerable attention because of the great diversity of products that can be produced from them.<sup>1</sup> In 1988, Trost reported the Pd(II)-catalyzed skeletal reorganization of enynes, in which two isomers of 1-vinylcyclopentenes, type I and II were formed.<sup>2</sup> While type I is produced via the cleavage of a C–C double bond, type II involves a double cleavage of a C–C double bond and a triple bond (Scheme 1).

In 1994, we reported that [RuCl<sub>2</sub>(CO)<sub>3</sub>]<sub>2</sub> also shows a high catalytic activity in the skeletal reorganization of enynes which led to the selective formation of type I products.<sup>3</sup> In this reaction, a CO atmosphere was crucial for the reaction to proceed. In fact,  $[RuCl_2(p-cymene)]_2$  and  $RuCl_3 \cdot xH_2O$  exhibited high catalytic activities only when the reaction was run under an atmosphere of CO. However, no catalytic activity was observed when the reaction was run under a N<sub>2</sub> or Ar atmosphere. In sharp contrast,  $[RuCl_2(CO)_3]_2$  showed catalytic activity even under N<sub>2</sub>. At this stage, we speculated that the role of CO is to increase the electrophilicity of the catalyst by coordination to a ruthenium center, which would facilitate an interaction between the alkyne and the catalyst because of its  $\pi$ -acidity.<sup>4</sup> Since then, a wide variety of electrophilic transition-metal complexes has been found to catalyze the cycloisomerization of enynes.<sup>1,5</sup> Some of these complexes exhibit a characteristic substrate specificity. In subsequent studies, we found that  $[Rh_2(O_2CCF_3)_4]$  also showed a high catalytic activity for the skeletal reorganization of enynes leading to the selective formation of type II products.<sup>5f,5g</sup>  $[Rh_2(O_2CCF_3)_4]$  was more reactive than  $[Rh_2(OAc)_4]$ , which again suggests that the electrophilicity of the catalyst is important for the reaction to proceed efficiently. The structure of  $[Rh_2(O_2CCF_3)_4]$  features a pair of rhodium atoms, each with an octahedral molecular geometry, defined by four acetate oxygen atoms (Scheme 2).

We were interested in the catalytic activity of  $[Ru_2(OAc)_4]X$ complex because it is structurally similar to  $[Rh_2(O_2CCF_3)_4]$ (Scheme 2).  $[Ru_2(OAc)_4]X$  was expected to have a unique catalytic activity because it is a Ru(II)–Ru(III) mixed-valence complex.<sup>6</sup> However, it has rarely been used in organic synthesis. The  $[Ru_2(OAc)_4]Cl$  complex was used only for hydrogenation,<sup>7</sup> the carbonylation of amines,<sup>8</sup> and the oxidation of alcohols<sup>9</sup> and amines.<sup>10</sup> We now report that  $[Ru_2(O_2CPh)_4(THF)_2]BF_4$ , a Ru(II)–Ru(III) mixed-valence complex, can be used as a catalyst



Scheme 1. Skeletal reorganization of enynes.



## Scheme 2. $[Rh_2(OCOCF_3)_4]$ vs. $[Ru_2(OAc)_4]X$ .



Scheme 3. Skeletal reorganization of enynes.

for the skeletal reorganization of 1,6-enynes when the reaction is run under an atmosphere of  $O_2$  or CO (Scheme 3).

The treatment of enyne 1 (0.2 mmol) with a catalytic amount of [Ru<sub>2</sub>(OAc)<sub>4</sub>(THF)<sub>2</sub>]BF<sub>4</sub> (0.01 mmol) in toluene (1 mL) at 80 °C under N<sub>2</sub> for 20 h gave the expected 1-vinylcyclopentene 2 in 56% yield. Similar to the Ru(II)-catalyzed skeletal reorganization of enynes, the yield was dramatically improved to 95% yield when the reaction was carried out under an atmosphere of CO, even for shorter reaction time (12 h). The yield was also improved to 65% when the reaction was run under  $O_2$  for 20 h. Kobayashi and co-workers observed that O<sub>2</sub> has a pronounced effect in [Mo<sub>2</sub>(OAc)<sub>4</sub>]-catalyzed Mukaiyama aldol reactions.<sup>11</sup> They proposed the intermediacy of an electrophilic catalytic species which is generated by the oxidation of  $[Mo_2(OAc)_4]$ under the reaction conditions. Other mixed-valence ruthenium complexes were examined under an atmosphere of O2. The use of [Ru<sub>2</sub>(O<sub>2</sub>CPh)<sub>4</sub>(THF)<sub>2</sub>]BF<sub>4</sub> gave 2 in 77% yield. However, a neutral complex, [Ru2(O2CPh)4]Cl was devoid of catalytic activity. The use of a Ru(III)-Ru(III)-Ru(III) complex, such as  $[Ru_3(OAc)_6(\mu^3-O)]OAc$  resulted in no yield of 2 at all. Next, various solvents were screened under O2 in the presence of [Ru<sub>2</sub>(O<sub>2</sub>CPh)<sub>4</sub>(THF)<sub>2</sub>]BF<sub>4</sub>. Almost no reaction occurred when cyclohexane, 1,4-dioxane, ethanol, and acetonitrile were used as the solvents. However, the use of 1,2-dichloroethane improved the yield of 2 (85% at 60 °C for 15 h under  $O_2$ ) (Scheme 4). The



Scheme 4.  $[Ru_2(O_2CPh)_4(THF)_2]BF_4$ -catalyzed skeletal reorganization of 1.

Table 1. Skeletal reorganization of 1,6-enynes<sup>a</sup>



<sup>a</sup>Reaction conditions: enyne (0.2 mmol),  $[Ru_2(O_2CPh)_4-(THF)_2]BF_4$  (0.01 mmol) at 60 °C in 1,2-dichloroethane (1 mL). <sup>b</sup>The reaction was run at 80 °C. E = COOEt.

use of 1,2-dichloroethane also improved the yield of **2** when the reaction was run under CO.

To obtain additional information regarding the active catalytic species, NMR and ESI-MS studies were performed. No change was observed when  $[Ru_2(O_2CPh)_4(THF)_2]BF_4$  was exposed to a N<sub>2</sub> atmosphere at 60 °C. In sharp contrast, ESI-MS showed a significant change under CO and O<sub>2</sub>. However, the structure of the active species could not be confirmed because of production of complex mixtures.



Scheme 5.  $[RuCl_2(CO)_3]_2$  vs.  $[Ru_2(O_2CPh)_4(THF)_2]BF_4$ .



Scheme 6.  $[Ru_2(O_2CPh)_4(THF)_2]BF_4$ -catalyzed skeletal reorganization of 17.

The results obtained for some enynes in the presence of  $[Ru_2(O_2CPh)_4(THF)_2]BF_4$  as the catalyst are summarized in Table 1. A simple enyne **3** gave the 1-vinylcyclopentene **4** only in low yields irrespective of the atmosphere used. However, the presence of an alkyl group at the internal olefinic carbon, as in **5** and **7**, resulted in a dramatic increase in product yields.<sup>12</sup> In the case of enynes containing a trisubstituted olefin, as in **11** and **13**, the reaction proceeded and high yields of type I products were formed exclusively.

We have already reported on the  $[RuCl_2(CO)_3]_2$ -catalyzed skeletal reorganization of enynes.<sup>4</sup> However, the catalytic activity of  $[RuCl_2(CO)_3]_2$  and  $[Ru_2(O_2CPh)_4(THF)_2]BF_4$  appear to be different. For example, **15** is one of the most reactive substrates in  $[RuCl_2(CO)_3]_2$ -catalyzed reactions, but no reaction occurred when  $[Ru_2(O_2CPh)_4(THF)_2]BF_4$  was used as the catalyst (Scheme 5).

An enyne having a nitrogen atom in the tether **17** gave a mixture of the 1-vinylcyclopentene derivative **18** and the bicyclic[4.1.0]heptene derivative **19**, the latter being the major isomer (Scheme 6).

In summary, we report on the skeletal reorganization of 1,6enynes leading to 1-vinylcyclopentene derivatives catalyzed by a mixed-valence Ru(II)–Ru(III) complex. The reaction gives optimal yields when run under an atmosphere of  $O_2$  or CO.<sup>13</sup>

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## **References and Notes**

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