

Communications

Catalytic Activity of Binuclear Ru-Complexes in Ring-Closing Metathesis

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Olefin metathesis has become one of the simplest and most effective synthetic methods for carbon-carbon double bond construction. Much of the recent successful progress in ring-closing metathesis stems largely from the availability of several well defined mononuclear Ru-complexes such as 1~4 (Figure 1).¹ On the other hand, numbers of binuclear and trinuclear molybdenum-based Schrock-type and ruthenium-based Grubbs-type complexes have also been developed, particularly, for the preparation of di- or tri-block, star-shape block copolymers.² Despite their potential for RCMs, to our best knowledge, no investigation has been made for RCMs with binuclear Ru-complexes.³ In the course of our investi-

gation on new-type of recoverable self-supported Hoveyda-type Ru-complexes,⁴ we found that binuclear Ru-complex 5 exhibited slightly higher catalytic activity than the corresponding mononuclear Ru-complex 2. This result turned our attention to binuclear Ru-complex for RCM. Herein we report catalytic activities of four different types of binuclear Ru-complexes 5~8 and, for comparisons, their corresponding mononuclear Ru-complexes 1~4, in RCM of *N,N*-bisallyl *p*-toluenesulfonamide. We also described our finding of the unusual inverse temperature dependency of the Hoveyda's 1st generation-type Ru-complexes 3 and 7.

The binuclear Ru-complexes 5 and 6, generating catalytically active binuclear Ru-methylidene species, have been synthesized according to our reported procedures.⁴ Other type of binuclear Ru-complexes 7 and 8, which could generate two catalytically active mononuclear species, were synthesized straightforwardly through the CuCl-assisted metathesis of the dimeric isopropoxystyrene having *p*-bismethylenepheryl

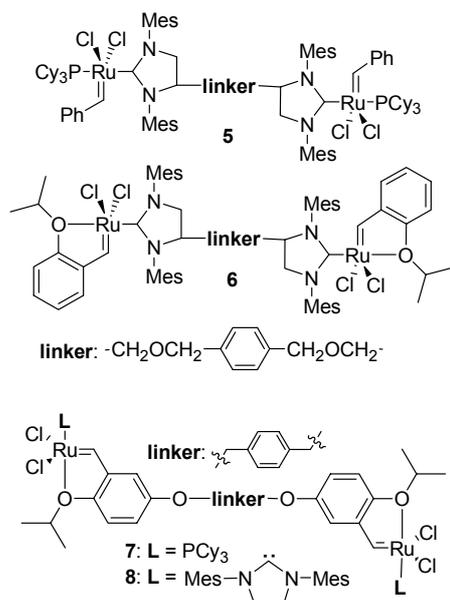
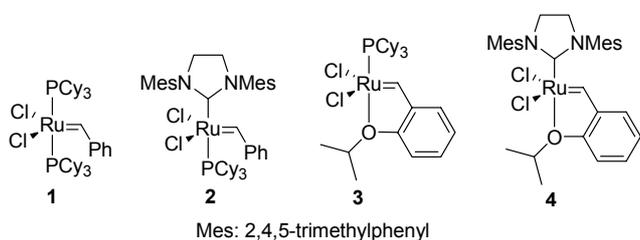


Figure 1. Mononuclear and binuclear Ru-complexes 1~8

Table 1. RCM of *N,N*-bisallyl *p*-toluenesulfonamide using Ru-complexes 1~8.

| Entry | Cat. | Temp. (°C) | Time | Conv. (%) |
|-------|------|------------|--------|-----------|
| 1 | 1 | RT | 30 min | > 98 |
| | | 40 | 15 min | > 98 |
| 2 | 2 | RT | 1.0 h | > 98 |
| | | 40 | 45 min | > 98 |
| 3 | 5 | RT | 2.0 h | > 98 |
| | | 40 | 30 min | > 98 |
| 4 | 3 | RT | 3.5 h | > 98 |
| | | 40 | 12 h | 74 |
| 5 | 7 | RT | 1.5 h | > 98 |
| | | 40 | 12 h | 85 |
| 6 | 4 | RT | 2.0 h | > 98 |
| | | 40 | 1.5 h | > 98 |
| 7 | 6 | RT | 4.0 h | > 98 |
| | | 40 | 2.0 h | > 98 |
| 8 | 8 | RT | 50 min | > 98 |
| | | 40 | 25 min | > 98 |

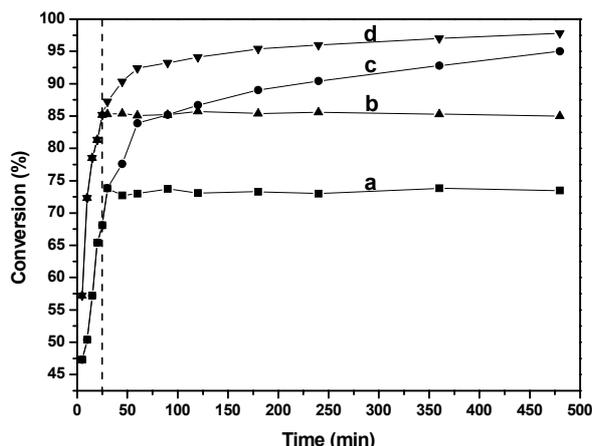


Figure 2. Reaction profiles for Ru-complexes **3** and **7**. Reaction at 40 °C (a) with **3**, (b) with **7**. Reaction at 40 °C for 30 min and then RT (c) with **3** and (d) with **7**.

linker with Grubbs' 1st-**1** and 2nd-generation Ru-complexes **2**, respectively (Figure 1). Catalytic activity of the mononuclear Ru-complexes **1**–**4** and binuclear Ru-complexes **5**–**8** were investigated for RCMs of *N,N*-bisallyl *p*-toluenesulfonamide using 5 mol % (based on Ru content) catalyst at room temperature and 40 °C. The results are summarized in Table 1.

As shown in Table 1, Grubbs 1st-generation catalyst showed the highest catalytic activity (Entry 1, Table 1). Comparisons between the catalytic activities of mononuclear Ru-catalyst **2** and the corresponding binuclear Ru-complex **5** indicated that mononuclear complex **2** exhibited about 2 times higher catalytic activity (Entries 2 and 3, Table 1). In contrast, the catalytic activity of the binuclear Hoveyda's 1st generation-type **7** is superior to the mononuclear **3** (Entries 4 and 5, Table 1). In the case of Hoveyda's 2nd generation-type Ru-complexes, the catalytic activity is dependent on the type of binuclear complex, *i.e.*, the binuclear complex **6** generating catalytically active binuclear Ru-methylidene complex exhibited lower catalytic activity than the mononuclear **4** whereas higher catalytic activity was observed with the complex **8** generating two catalytically active Ru-methylidene species (Entries 6, 7 and 8, Table 1). At high reaction temperature, the binuclear complexes **5** and **8** exhibited higher catalytic activity than the corresponding mononuclear complexes **2** and **4**. In contrast, the Hoveyda's 1st generation-type Ru-complexes **3** and **7** exhibited much lower catalytic activity at higher reaction temperature. Thus, the RCMs with Ru-complexes **3** or **7** at 40 °C could not be completed even after 12 h. In order to know that the decreased catalytic activity of Ru-complexes **3** and **7**

at high temperature is associated with the decomposition of the catalysts, we carried out the reaction at 40 °C for 25 min first, accomplishing 74% (Figure 2a) and 85% conversions (Figure 2b), respectively, and then, the temperature was cooled to room temperature and continued the reaction. As shown in Figure 2, the catalytic activity of the catalysts **3** (Figure 2c) and **7** (Figure 2d) restored. These results clearly indicated that the active catalytic species are stable at 40 °C. Although it is not clear yet the reasons for this kind of inverse temperature dependent behaviors, the uncompleted conversions at 40 °C to the equilibrium between ring-closing and ring-opening processes.

In summary, we have investigated the catalytic activity of binuclear Ru-complexes **5**–**8** exhibiting comparable or higher activity to those of the corresponding mononuclear Ru-complexes in the ring-closing metathesis reaction. We also observed for the first time that the catalytic activity of both monomeric and dimeric Hoveyda-Grubbs first-generation Ru-complexes showed inverse temperature dependency. Further studies on elucidation the origin of this unusual temperature dependency are underway.

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