

Monolayer protected Au cluster (MPC)-bound Ru–carbene complex: synthesis and its catalytic activity in ring-closing olefin metathesis

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Received 4 March 2005; revised 6 April 2005; accepted 15 April 2005

Abstract—Monolayer-protected gold cluster (Au-MPC)-bound Ru–carbene complex (MPC-7) has been synthesized and examined its catalytic activity in ring-closing olefin metathesis. The MPC-7 showed almost the same catalytic activity with that of simple molecules (Grubbs Ru-complex **1b** and the thioacetate-functionalized Ru-complex **8**) and reused several times.

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The modification of monolayer-protected nanosize metal clusters, especially Au clusters (Au-MPCs) by the incorporation of a functionalized thiol or disulfide is of potential significance for the expansion of chemical and biological applications of these materials.¹ Based on the reactive ω -functional groups, a variety of organic reactions such as nucleophilic substitution and addition reactions, coupling, and polymerizations etc. have been extensively studied.² However, reports concerning MPCs coated with thiols or disulfides bearing catalytically active species, especially metal-complexes at terminal position are quite limited.³ Utilization of nanoparticle-supported catalysts may provide a number of advantages: (i) nanometer-sized MPC (usually in the 2–25 nm size range) behaves like homogeneous, but can be precipitated by varying solvents allowing an easy separation of the catalyst; (ii) The catalysts are readily exposed on the surface of the metal clusters, and expected to show high catalyst activity, which would be comparable to the parent homogeneous catalysts; (iii) Moreover, in contrast to polymer-supported catalysts, the MPC-supported catalysts are amenable to characterization by ¹H NMR in solution. Herein, we report synthesis of a novel Au-MPC-bound Ru–carbene complex and its catalytic activity in ring-closing olefin metathesis.

The ring-closing olefin metathesis (RCM) catalyzed by Ru-complexes, most notably the Grubbs-type Ru alkylidenes **1a** and **b** and Hoveyda's **2a** and **b** (Fig. 1), has tremendous impact in synthetic organic chemistry.⁴ Hence, various kinds of support materials including polymers,⁵ dendrimers,⁶ and most recently ionic liquids⁷ and fluorinated polymer⁸ have already been utilized for the development of robust and recyclable Ru-catalysts for RCM. However, no attempts have been made to immobilize the Ru–carbene complex onto the Au-MPCs.

Scheme 1 shows the synthesis of Au-MPC-bound Ru–carbene complex. The required styrene-functionalized thiol **4b** could be obtained by *O*-alkylation of the 5-hydroxy-2-isopropoxystyrene **3^{sf}** with 1-bromo-12-thioacetatyldecane⁹ followed by the hydrolysis of the resulting thioacetate **4a**. Subsequently, we accomplished an associative place-exchange reaction by dissolving the octanethiol-passivated Au-MPC **5** (average core diameter: ~2.5 nm), which was prepared according to the detailed protocol reported by Murray and co-workers,¹⁰

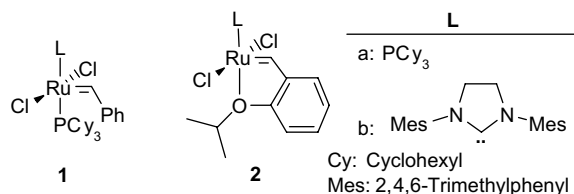
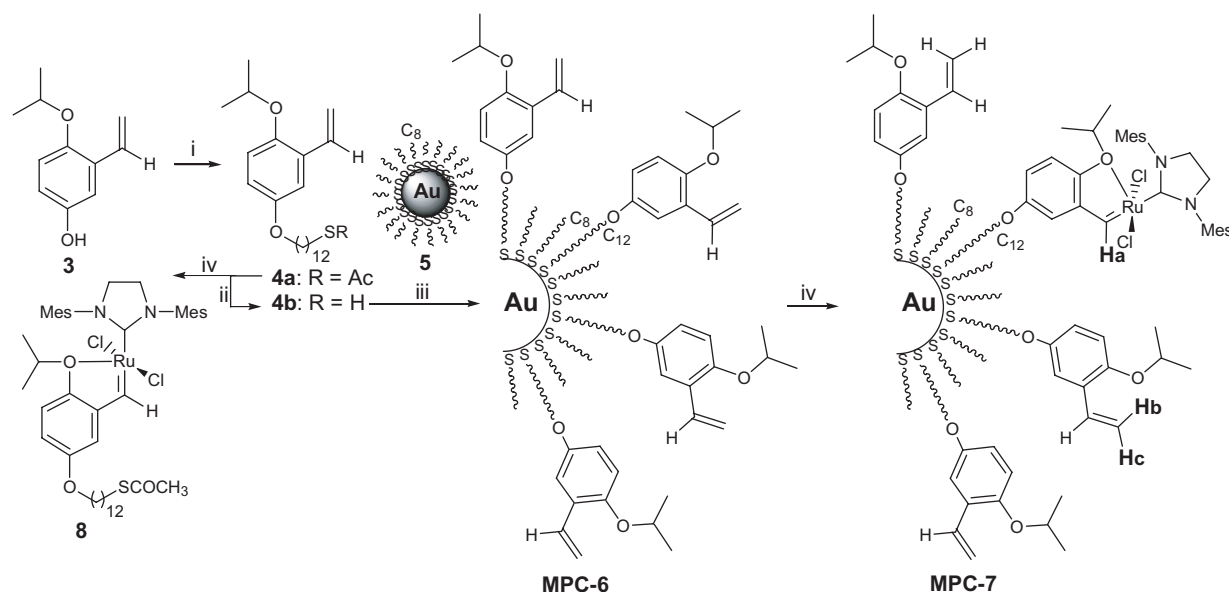


Figure 1. Typical Ru–carbene complexes used for the RCM of olefins.

Keywords: Monolayer; Gold cluster; Ru–carbene complex; Metathesis.

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Scheme 1. Synthesis of Au-MPC-bound Ru-carbene complex (MPC-7). Reagents and conditions: (i) NaH/THF/Br(CH₂)₁₂SCoCH₃, rt, 30 min, 87%; (ii) aqueous NaOH, EtOH, rt, 1 h, 98%; (iii) compound **5**, CH₂Cl₂, rt, 20 h; (iv) compound **1b**, CuCl, CH₂Cl₂, reflux, 2 h, **8** (85%).

and styrene-functionalized thiol **4b** in dichloromethane. After removing the solvent, the resulting black solid was washed several times with anhydrous, degassed ethanol to give the MPC-6. The ligand exchange could be confirmed by ¹H NMR spectrum analysis, in which the resonance signals of the vinyl (δ 5.70 and 5.23 ppm) and phenyl ring protons (δ 6.75 and 7.03 ppm) of the styrene moiety appeared, and revealed that the obtained MPC-6 comprises a 3:1 mixture of octane- and styrene-functionalized thiolates.¹¹ Treatment of MPC-6 with second generation Grubbs Ru-complex **1b** in the presence of CuCl^{4d} resulted in the exchange of the styrene groups to deliver the black, nano-size MPC-7, which was washed thoroughly with ethanol to remove the residual **1b**. Under the same reaction condition, the parent homogeneous Ru complex **8** could also be synthesized by reaction of the thioacetate **4a** with **1b** in 85% yield. Formation of Ru-complex in MPC-7 and **8** can clearly be confirmed by the ¹H NMR spectra analyses. In ¹H NMR spectrum of MPC-7, the characteristic Ru=CH proton (**Ha**) resonated at 16.44 ppm. The ratio of the integration area between the **Ha** and **Hb** (or **Hc**) indicates that one-fourth of the vinyl moiety presented in MPC-6 formed Ru complex. The MPC-supported Ru-carbene complex is soluble in dichloromethane and toluene, but insoluble in methanol, ethanol, and diethyl ether. Elemental analysis indicated that 0.18 mmol/g of Ru incorporated in the MPC-7. The transmission electron microscopy (TEM) measurements show that the size of Au core (average 2.4 nm) retained during the place-exchange and incorporation of Ru species (Fig. 2a).

To examine the catalytic activity of the Au-MPC-bound Ru-carbene complex (MPC-7), the ring-closing metathesis was carried with **9a** as model substrate using 5 mol% of catalyst in dichloromethane at 40 °C. As shown in Table 1, the catalytic activity of the MPC-7 (entry 3) is quite comparable with those of the Grubbs Ru-complex **1b** (entry 1) and the thioacetate-functional-

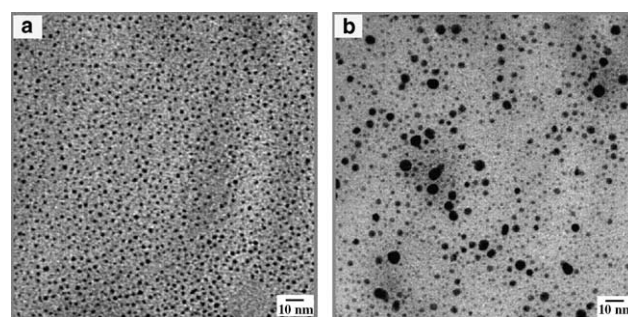


Figure 2. TEM images of (a) MPC-7 as prepared and (b) after 7th cycle (entry 9 in Table 1).

ized Ru-complex **8** (entry 2), and all reactions afforded the ring-closed product **10a** in quantitative yields. To assess the reusability of the MPC-bound Ru-carbene complex MPC-7, the catalyst was recovered from the first run (entry 3 in Table 1),¹² and used then in subsequent reactions. It has been found that the catalytic activity of the recovered MPC-7 was retained during the first four runs (entries 3–6), but slightly dropped in 5th (entry 7) and 6th cycles (entry 8). After, 6th cycle, the catalytic activity decreased dramatically, and the reaction in 7th cycle was not completed even in extended reaction time (12 h) (entry 9). Noteworthy observation is that the soluble MPC-7 in dichloromethane became insoluble during the reaction in 7th run (entry 10), and precipitated out. The TEM analysis of the insoluble particles obtained from the 7th run (Fig. 2b) clearly indicate that the size of the particles has been increased (average diameter: 8.0 nm).¹³ Based on these considerations, it could be assumed that the coated monolayers on the gold surfaces are destroyed, and once they start desorption from the gold surface, the coated monolayers could destruct dramatically leading to the aggregation of the gold clusters, and the catalytically active Ru-carbene complex could be decomposed, and lose their catalytic

Table 1. Ring-closing metathesis of dienes **9a–c**

Entry	Cycle	Cat.	9	Conv (%) ^a
1 ^b	1st	1b	9a	>98
2 ^c	1st	8	9a	>98
3 ^d	1st	MPC-7	9a	>98
4	2nd	MPC-7	9a	>98
5	3rd	MPC-7	9a	>98
6	4th	MPC-7	9a	98
7	5th	MPC-7	9a	85
8	6th	MPC-7	9a	80
9 ^e	7th	MPC-7	9a	20
10	1st	MPC-7	9b	>98
11	1st	MPC-7	9c	>98

^a Determined by ¹H NMR and reactions carried out for 1.5 h otherwise noted.

^b Reaction carried out for 3 h.

^c Reaction carried for 30 min.

^d For entries 3–8, the catalyst was recovered for the next run.¹²

^e Reaction carried for 12 h.

activity. Finally, we examined the catalytic activity of the MPC-7 for other substrates **9b** and **c**, and afforded the corresponding products **10b** (entry 10) and **c** (entry 11) in quantitative yields.

In conclusion, we have synthesized a novel monolayer-protected gold nanoparticles-bound Ru–carbene complex MPC-7, which showed high reactivity and high levels of reusability in ring-closing olefin metathesis suggesting that the monolayer-protected nanoparticles could have a high potential as support-materials for the recyclable catalysts. Studies on MPC-supported catalysts for other catalytic reactions are under progress.

Acknowledgements

The authors thank financial support from National Research Laboratory and Future Core Technology Program at KIST, Center for Molecular Design and Synthesis at KAIST.

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- The ratio of 3:1 was determined by comparing the integrated areas for the vinyl protons of **4b** and the poly(methylene) chains for both **4b** and octanethiolate.
- The dichloromethane solvent was removed, and the product **10a** was dissolved in methanol, and the precipitated MPC-7 was isolated, dried, and used for the next run.
- In UV–vis absorption spectra (1 mg sample in 10 mL of CH₂Cl₂) of the MPC-7 recovered until 6th cycle, the λ_{max} (~520 nm) and absorbance (0.60) were almost retained. However, no λ_{max} could be observed from the MPC-7 after 7th cycle, which may be largely due to the poorer solubility by the formation of aggregates as they demonstrated in TEM.