

Ring Closing Metathesis of Diallylmalonate

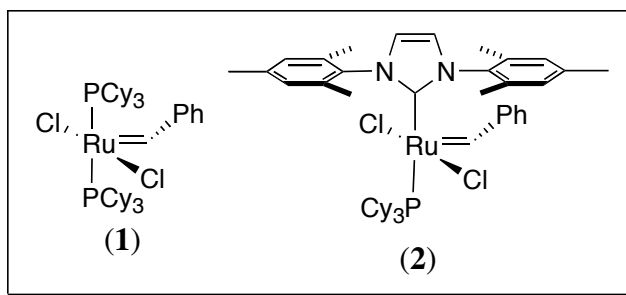
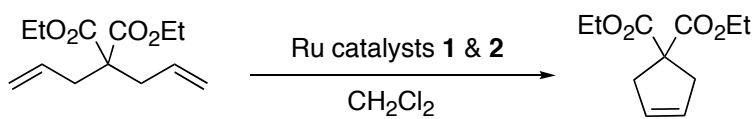
Introduction

The goal of the second part of our metathesis project is to demonstrate the effectiveness of your synthetic complex **2** for an olefin ring-closing reaction, and to compare the reactivity of complexes **1** and **2**.

Experimental Section

This experimental section is based on work by Prof. Steve Nolan at the University of New Orleans, and Prof. Melanie Sanford at the University of Michigan, who are gratefully acknowledged for sharing this information with us.

Part B: RCM of diallylmalonate



Safety Recommendations: Diallylmalonate and the product are harmful if swallowed, inhaled, or absorbed through skin.

Chemical Data: Complete this table *before* running the experiment.

Compound	FW	Amount	Mmol	Mp [°C]	Density
diallylmalonate					
Ru-catalyst 1					
Ru-catalyst 2					

Required Equipment: Glassware for this reaction – 25 mL flasks containing a stir bar – should be dried in the oven for at least 8 h before starting the experiment. Glove bag. Septa. Magnetic stirrer.

RCM Reaction. A solution of catalyst **1** (16 mg, 0.02 mmol) in dry degassed CH₂Cl₂ (10 mL) was prepared under nitrogen. Diethyl diallylmalonate (100 mg, 0.416 mmol) was added and the reaction mixture was stirred under nitrogen for 1 h at room temperature. After addition of diethyl ether (30 mL), the mixture was filtered through a plug of silica gel. The solvent was removed on the rotovap, and a crude GC-MS spectrum of a diluted (diethyl ether) aliquot was acquired. The product was also analyzed by thin-layer chromatography on silica gel, and if necessary purified by column chromatography. Repeat this protocol with the appropriate amount of complex **2**.

Characterization of Product. GC/MS; ¹H NMR; IR. How do your data compare to the literature values of the product?

Questions. **1.** How do you determine the optimal conditions for purification of the product? **2.** How do you find out which complex is more reactive? **3.** In addition to the cyclic product, what other organic compound is formed? **4.** Based on your knowledge of le Chatlier's principle and what you know about the other organic product of this reaction, how could you modify the conditions to accelerate the rate/improve the yield of this reaction? **5.** In *J. Am. Chem. Soc.* **2002**, *124*, 14848, Ru-catalysts are used for 3 different reactions. If diallylmalonate would be used as a substrate, what would the corresponding products look like?

References:

- T. A. Kirkland, R. H. Grubbs, *J. Org. Chem.* **1997**, *62*, 7310.
Schwab *et al.* *J. Am. Chem. Soc.* **1996**, *118*, 100.
Sanford *et al.*, *J. Am. Chem. Soc.* **2001**, *123*, 6543.
Wipf *et al.*, *J. Am. Chem. Soc.* **2002**, *124*, 14848.