



## Synthesis and reactivity of oxygen chelated ruthenium carbene metathesis catalysts



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### ARTICLE INFO

#### Article history:

Received 12 November 2013

Received in revised form

8 January 2014

Accepted 17 January 2014

#### Keywords:

Olefin metathesis

Ruthenium

*N*-Heterocyclic carbenes

Homogeneous catalysis

### ABSTRACT

The rate of initiation of Hoveyda catalysts is affected by the electronic and steric effects that act upon the Ru···O coordination. In order to boost the activity of Hoveyda catalysts, a series of new oxygen chelated ruthenium carbene metathesis catalysts containing an *N*-heterocyclic carbene (NHC) and a carbonyl group has been developed, and their catalytic activities for olefin metathesis reactions were investigated. The aliphatic end groups of complexes (H<sub>2</sub>IMes)(Cl)<sub>2</sub>Ru=C(H)[(C<sub>6</sub>H<sub>3</sub>X)OCH(Me)(C(O)OEt)(X = H, OMe, Me, NO<sub>2</sub>)] were functionalized by the attachment of a straight-chain ester. The X-ray structures of complex (H<sub>2</sub>IMes)(Cl)<sub>2</sub>Ru=C(H)[(C<sub>6</sub>H<sub>4</sub>)OCH(Me)(C(O)NMe<sub>2</sub>)] showed that the carbonyl oxygen of the amide and the terminal oxygen of the benzylidene ether are both coordinated to the metal to give an octahedral structure. However, the carbonyl oxygen of complexes (H<sub>2</sub>IMes)(Cl)<sub>2</sub>Ru=C(H)[(C<sub>6</sub>H<sub>3</sub>X)OCH(CH<sub>2</sub>C(O)OCH<sub>2</sub>)(X = H, OMe)] does not coordinate to the metal due to the steric effect of the lactone. All these complexes were used as catalysts for olefin metathesis reactions and all exhibited excellent performances for the ring-closing metathesis (RCM) of diethyl diallylmalonate at 30 °C. The initiation rate of these catalysts was higher than that for the Hoveyda catalyst ((H<sub>2</sub>IMes)(Cl)<sub>2</sub>Ru=C(H)(C<sub>6</sub>H<sub>4</sub>-2-<sup>*O*</sup>Pr)) and these complexes are also active for cross metathesis (CM).

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### 1. Introduction

Since the discovery of well-defined modern ruthenium catalysts **1–4** (Chart 1) [1], olefin metathesis as one of the most important tools for constructing carbon–carbon double bonds has been widely used in organic synthesis, materials science, and biochemistry [2]. Among these complexes, Grubbs second-generation ruthenium carbene catalyst **2** possesses a high activity and an excellent tolerance for a variety of functional groups. Ruthenium-benzylidene catalyst **4** which bears *N*-heterocyclic carbene (NHC) ligand, exhibits extraordinary activity and stability was introduced by Hoveyda and coworker [1c]. It is widely used in reuse and immobilization of the catalyst [3–5]. However, a large isopropoxy group and the donation of an electron from <sup>*t*</sup>PrO to ruthenium cause this catalyst to initiate more slowly than Grubbs catalyst **2**.

In 2002, Wakamatsu and Blechert synthesized complex **5** by modifying the neighboring bulky phenyl group [6]. This phenyl

ruthenium catalyst lead to greatly increased initiation rates for different metathesis reactions even at 0 °C. Around the same time, Grela et al. developed complex **6** which has an electron-withdrawing substituent (a nitro group) [7]. Under very mild conditions (even at 0 °C) it was successfully applied to various types of olefin metathesis (ring-closing metathesis, cross metathesis and enyne metathesis). Both complexes **5** and **6** destabilize the oxygen/metal interaction which favors faster access to the formation of the 14-electron Ru carbene species; these results in increasing catalytic activity [8].

However, as mentioned by Conrad et al. [9], the global efficiency of an olefin metathesis catalyst not only has a high initiation rate and a high selectivity, but also has extraordinary stability and the stability of the precatalyst plays an important role. In order to boost the stability of the catalyst, many improvements have been made including changing the *N*-heterocyclic carbene [10] and the leaving group [11]. So, many highly efficient and stable Ru carbene metathesis catalysts have been designed based on complex **4** [12,13].

Complex **7a** and **7b** were developed by Bieniek et al., in 2006 [12b]. The aliphatic end groups of the complexes were functionalized by attaching an ester group which enhanced the leaving group

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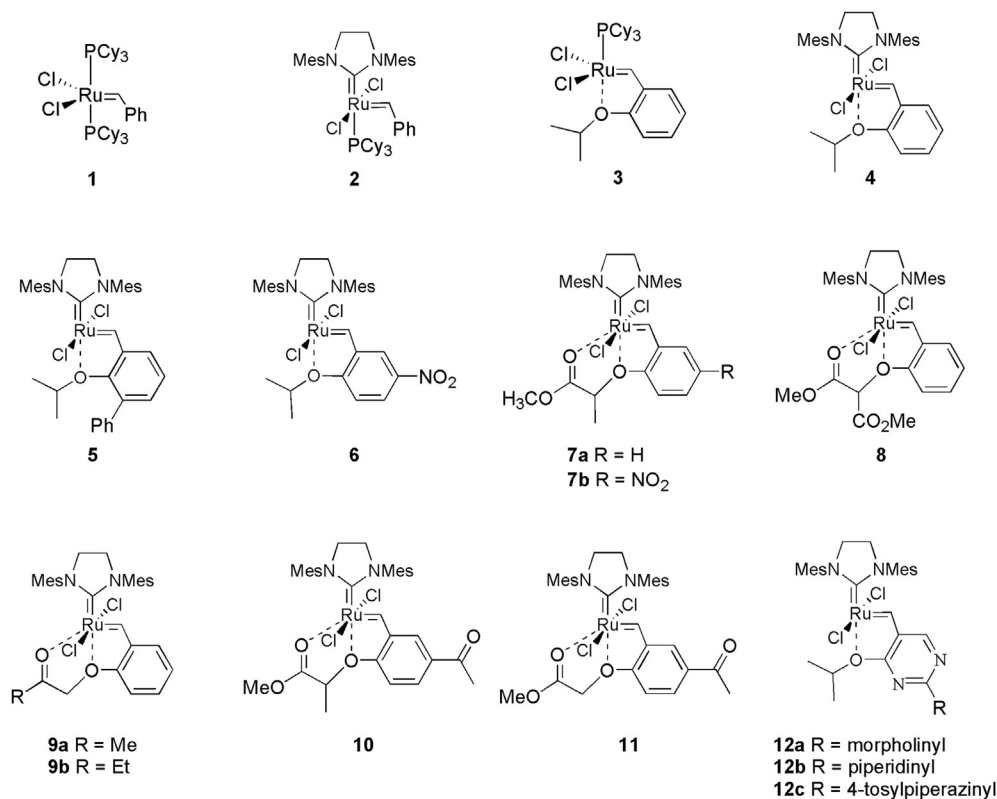


Chart 1. Ruthenium metathesis catalysts.

properties of the styrenyl ether. X-ray results showed that the carbonyl oxygen of the ester group in these complexes coordinated to the metal. Furthermore, complex **7b** which has an electron withdrawing NO<sub>2</sub> group gave high turnover numbers.

The rate of initiation of chelated complexes is affected by the electronic and steric effects that act upon the Ru···O coordination. In 2011, Bieniek et al. synthesized a series of complexes **8–11** with different substituents (an ester group, a ketonic group, or a malonic

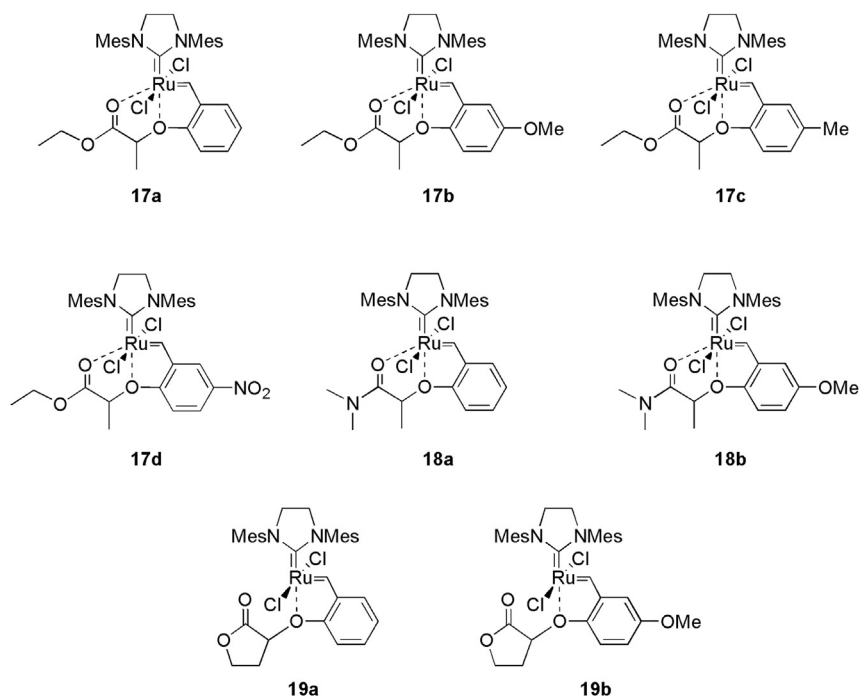


Chart 2. New oxygen chelated ruthenium carbene metathesis catalysts.

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