



Stability and activity of *cis*-dichloro ruthenium olefin metathesis precatalysts bearing chelating sulfur alkylidenes



Eyal Tzur^{a,*}, Elisa Ivry^b, Charles E. Diesendruck^b, Yuval Vidavsky^b, Israel Goldberg^c, N. Gabriel Lemcoff^b

^a Department of Chemical Engineering, Shamoon College of Engineering, Ashdod 77245, Israel

^b Chemistry Department, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

^c School of Chemistry, Tel-Aviv University, Tel-Aviv 69978, Israel

ARTICLE INFO

Article history:

Received 23 March 2014

Received in revised form

16 June 2014

Accepted 25 June 2014

Available online 16 July 2014

Keywords:

Ruthenium complexes
cis-Dichloro configuration
Latent catalysts
Olefin metathesis
Sulfur chelation
Metallacycle aromaticity

ABSTRACT

S-Chelated Grubbs type complexes are usually found in their stable *cis*-dichloro conformation. These precatalysts are usually latent and necessitate external stimuli to promote olefin metathesis reactions. Herein we report the synthesis of new S-chelated ruthenium complexes, by a simple exchange of the benzylidene to an alkylidene chelating ligand. The structure of the complexes was studied by NMR spectroscopy, single crystal X-ray diffraction and DFT calculations. The new complexes were tested in a series of olefin metathesis reactions and were found to be the first *cis*-dichloro ruthenium precatalysts that are active at room temperature. The observed differences in reactivity and structure between the alkylidene complexes and their benzylidene counterparts highlight the important influence aromaticity may have on the stability and activity of chelated Grubbs type complexes. The findings may also have implications to develop alternative strategies to stabilize, or destabilize, other organometallic complexes bearing relevant chelating ligands.

© 2014 Elsevier B.V. All rights reserved.

Introduction

Olefin metathesis [1] has greatly influenced many areas of organic synthesis, among them, the production of polymers [1f,2], natural products [1f,3], drugs [4] and chemical commodities from renewable resources [5]. Much of this progress has been due to the constant development of more reactive and stable catalysts, a very active field of research that has certainly afforded impressive achievements [1e,g,6]. For example, in applications related to the preparation of thermosets, intimate control over the reaction initiation and kinetics is essential in order to obtain homogenous materials featuring the desired mechanical properties [7]. With this in mind, we recently developed a series of sulfur chelated ruthenium olefin metathesis precatalysts which display dormant behavior [8]. The sulfur–Ru bond is remarkably strong, thus allowing for exquisite control over precatalyst initiation [8b,c]. Unexpectedly, these complexes disclosed a *cis*-dichloro configuration, opposed to the *trans*-dichloro conformation typically observed for commercial catalysts (Fig. 1). Even though different *cis*-dihalo

oxygen [9], halogen [10] and nitrogen [11] chelated complexes, which are active in room temperature have been reported, to date, all sulfur chelated precatalysts were found to be latent in several olefin metathesis applications at room temperature and could be activated by the use of heat [8a–c,e] or light [8d].

In order to control the initiation and performance of S-chelated precatalysts both steric and electronic effects may be harnessed. For example, the addition of a bulky group made compounds **2** and **3c** to be the most active within their series (Fig. 2) [8b,d]. These studies led to the conclusion that only the *trans*-dichloro isomer is active, while the *cis*-dichloro isomers are latent. In addition, electronic effects were also used in order to tune the S–Ru bond dissociation and affect catalyst efficiency. Thus, addition of a strongly electron withdrawing trifluoromethyl group to the sulfur atom formed *cis*-dichloro complex **4** (Fig. 2), which turned out to be the fastest S-chelated catalyst after isomerization (either by light or heat); competing in reaction rates with the popular O-chelated catalysts [8e]. Interestingly, when using a chelating sulfoxide instead of a thioether, the *trans*-dichloro complex was obtained as the most stable isomer in CH₂Cl₂ solution (**5**, Fig. 2), which was expectedly active towards ring-closing metathesis (RCM) and enyne metathesis reactions at ambient temperatures [12].

* Corresponding author. Tel.: +972 546813479.

E-mail address: eyalt@sce.ac.il (E. Tzur).

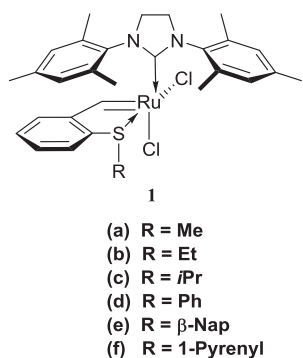


Fig. 1. *cis*-Dichloro ruthenium sulfur complexes 1.

Recently, Grela and coworkers studied the effect of the aromaticity of the 5-membered metallacycle ring in several oxygen-chelated naphthalene-based analogs of Hoveyda type catalysts [13]. Their results indicated that a stronger metallacyclic aromatic character increased chelate stability and inhibited precatalyst initiation. Therefore, in an attempt to further explore the role of aromaticity in chelated ruthenium catalysts, we decided to reduce metallacycle aromaticity by the simple approach of using an alkylidene instead of a benzylidene ligand. A literature survey reveals that alkylidene chelated complexes have been prepared in the past; for example, the 6-membered nitrogen chelated alkylidene complexes studied by Van der Schaaf and Grubbs [14], but the oxygen chelated alkylidene (5 and 6-membered) analogs were not stable enough to be isolated [15]. We expected that the stronger sulfur–ruthenium bond would still allow the formation of this binding form, albeit the reduced stability due to lack of aromaticity.

Results and discussion

Synthesis of ruthenium complexes

The synthesis of thioethers **7a** and **7b** are described in Scheme 1. 4-Bromobutene was added to a mixture of thiol **6**, potassium carbonate and 18-crown-6 in acetone and refluxed overnight to afford

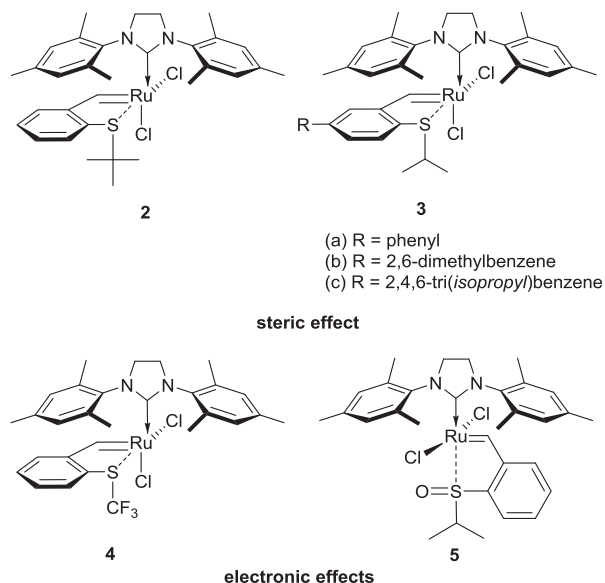
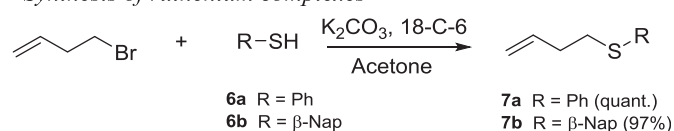


Fig. 2. Steric and electronic effects in sulfur chelated ruthenium complexes.

Synthesis of ruthenium complexes



Scheme 1. Synthesis of thioethers **7a** and **7b**.

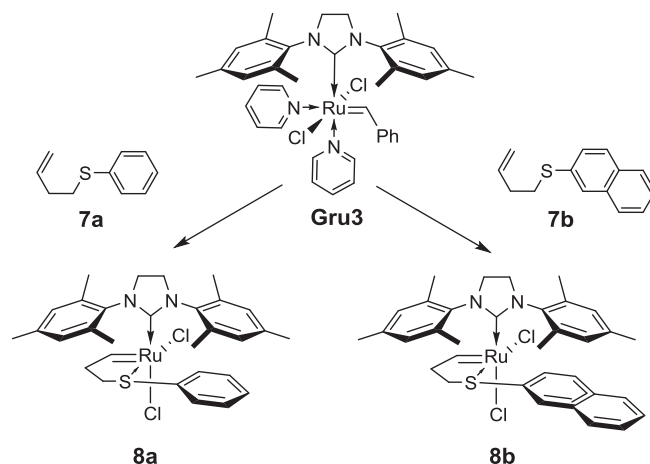
the desired products **7** in quantitative yields after isolation. Consecutively, alkylidene complexes **8a** and **8b** were obtained by treatment of Grubbs 3rd generation catalyst (**Gru3**) [16] with **7a** and **7b** respectively in CH_2Cl_2 (Scheme 2).

Structural characterization of the prepared complexes

Complexes **8a** and **8b** were fully characterized by NMR spectroscopy and HRMS (ESI) (see Supporting information) analyses. The solid-state structure of complex **8a** was also studied using single crystal X-ray diffraction (Fig. 3).

The NMR spectra obtained were analyzed to understand the structure of ruthenium complexes **8a** and **8b** in solution. As typically observed for the *cis*-dichloro configuration, every proton and methyl group in the molecule was clearly resolved. When comparing the spectra of **8a** and **8b** to their benzylidene analogs **1d** and **1e** [8b,d], a significant difference in the chemical shift of the corresponding aromatic mesitylene protons can be observed. The most upfield mesitylene proton appears at 6.06 ppm for both **1d** and **1e** compared to 6.70 ppm (for **8a**) and 6.65 ppm (for **8b**). This change is associated with a diminished anisotropic effect in **8a** and **8b** due to the absence of the aromatic moiety in the chelated sulfur ligand. Moreover, a minor deshielding of the carbene proton can be observed in **8a** and **8b**. The proton appears at lower field (17.45 and 17.51 ppm) when compared to **1d** and **1e** (17.21 and 17.14 ppm) respectively.

Table 1 presents a comparison between selected bond lengths and angles of **8a** and its analog **1d** [8b]. Notably, despite the fact that complex **8a** is active at room temperature (*vide infra*), it exhibits a shorter sulfur–ruthenium bond compared to latent **1d**. This reduced bond length can be explained by the lack of aromaticity in the chelated ring – double bonds in aromatic rings being longer than standard double bonds [17]. Another important deviation in the structure between **1d** and **8a** can be found in the conformation of the five membered metallacycle. While in **1d** all the atoms comprising the cycle are found in the same plane, **8a** shows a



Scheme 2. Synthesis of precatalysts **8a** and **8b**.

Download English Version:

<https://daneshyari.com/en/article/1323782>

Download Persian Version:

<https://daneshyari.com/article/1323782>

[Daneshyari.com](https://daneshyari.com)