

In Focus

Ruthenium in Olefins Cross-Metathesis Reactions

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Rutênio nas Reações de Metátese Cruzada em Olefinas

Resumo: Reações de metátese são aquelas onde ocorre rearranjo de ligações π . Elas ocorrem principalmente com alcenos, incluindo as reações de metátese cruzada. Utilizando a metátese como ferramenta sintética, é possível obter novas olefinas com estereoquímica definida, de modo rápido e limpo. Para que isso possa acontecer, entram em cena os catalizadores, entre os quais se destacam os constituídos de Rutênio, como os catalizadores de Grubbs, de Hoveyda e novos catalizadores desenvolvidos a cada dia.

Palavras-chave: Metáteses; alcenos; rutênio; catalizadores.

Abstracts

Metathesis reactions happen with the rearrangement of π bonds. This kind of reaction occurs mostly with alkenes, including the cross-metathesis reactions. Using metathesis as a synthetic tool, we can obtain new olefins with defined stereochemistry, in a clean and fast way. For this to happen, come into action certain catalysts. Among them are those containing Ruthenium like the Grubbs and the Hoveyda catalysts, as well new catalysts being developed.

Keywords: Metathesis; catalysts; ruthenium; alkenes.

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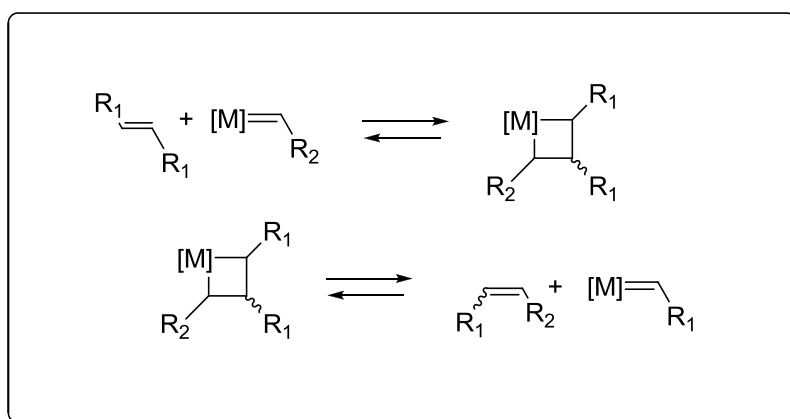
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1. Introduction

Olefins cross-metathesis reactions are metathesis reactions where two alkenes exchange fragments. These reactions are an alternative to others forms of carbon-carbon bond formation. They are an advance because of a series of reasons like the necessity of only one to five percent of catalyst and the obtained good yields. These reactions conditions are mild, the reaction

times are short and often ethylene is the only by-product generated. Olefins are the substrates needed to perform cross metathesis reactions; they are relatively easy to prepare, so being used as substrates.^{1,2}

These transformations can happen because a metal alkylidene and an olefin make together a cyclic intermediate with four atoms. The intermediate is broken to form a new metal alkylidene and the olefin product. These steps are a cycloaddition and a retrocycloaddition respectively.³



Scheme 1. General mechanism of cross-metathesis reactions

2. Ruthenium catalysts

Ruthenium catalysts are stable in the

presence of air and water. They are compatible with alcohols, carboxylic acids and aldehydes.¹

There are some commercial ruthenium

catalysts like the Grubbs catalysts from first (1) and second (2) generations, and Hoveyda-Grubbs catalysts also from first (3) and second (4) generations. In Figure 1, it is possible to see these catalysts and their structural differences.

Both the Grubbs and the Hoveyda-Grubbs

second generation catalysts have N-heterocyclic carbene ligands that are strong σ -donor. The role of these ligands is to stabilize the future complex with the olefin. Therefore, the catalytic cycle becomes more efficient.⁴

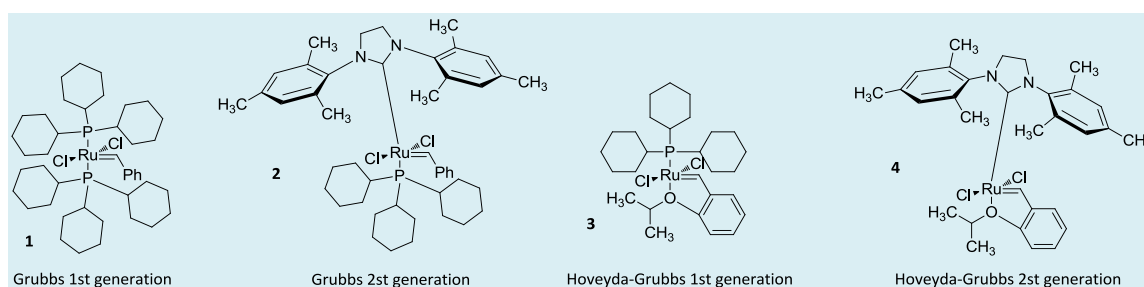


Figure 1. Some of the traditional ruthenium catalysts developed by Grubbs and Hoveyda

Despite the more efficient catalytic cycle, there is still a challenge in cross-metathesis reactions and this is stereochemistry. The majority of catalysts drive the reaction to the formation of E olefins, because it is the thermodynamically favorable product. When the Z olefin product occurs, it is isomerized.⁵

The groups of Grubbs and Hoveyda have been searching for new ruthenium catalysts capable of bringing kinetic control, inducing the formation of Z olefins. They have prepared these catalysts with bulky ligands

that force the substituent to the opposite side in the cyclic intermediate.⁵

In figure 2, it is possible to see the differences between the Ruthenium catalyst linked to two chlorine atoms, favoring the formation of the E olefin in the cyclic intermediate; and the catalyst linked to a bidentate anionic bulky ligand, favoring the Z olefin formation. In the first case, the electronic repulsion between the two chlorine atoms favors the cyclic intermediate with R1 and R2 in the anti conformation.⁵

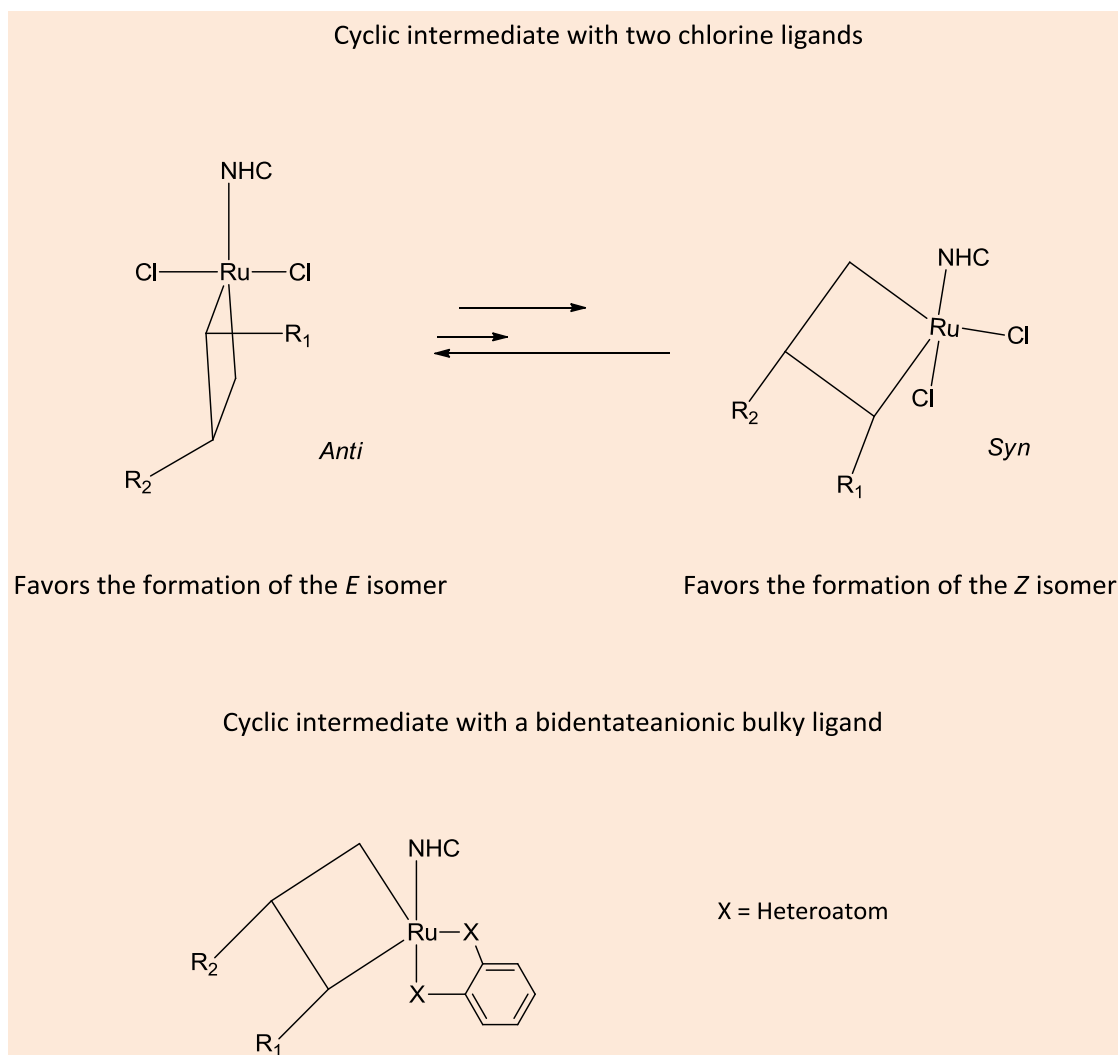
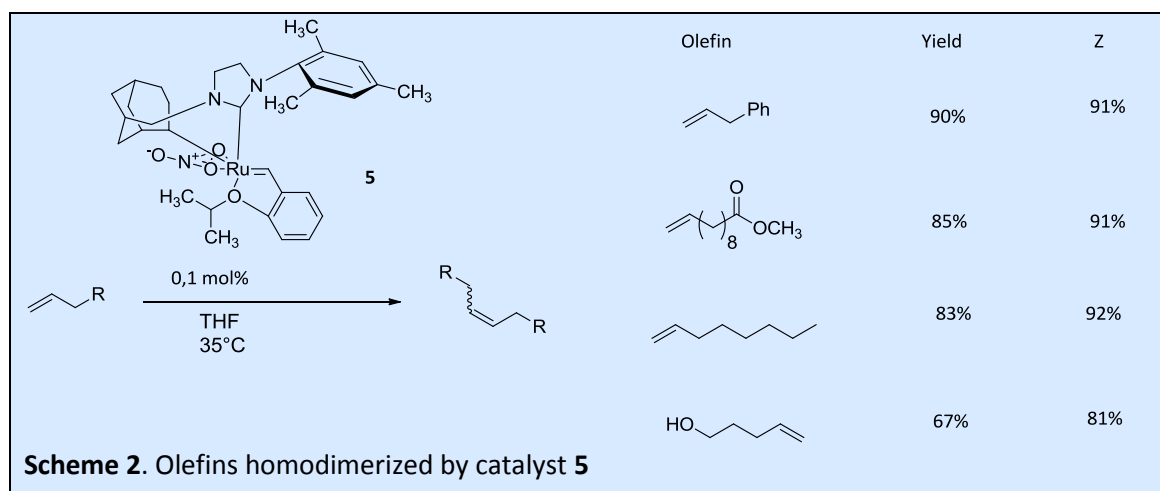


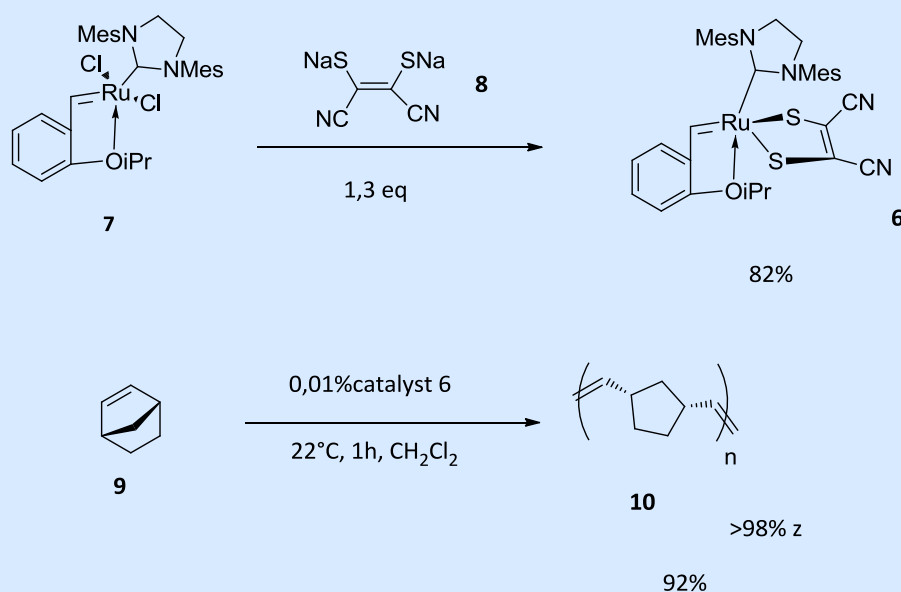
Figure 2. Cyclic intermediate with different ligands and the E/Z olefin formation

3. Experimental Procedures

A catalyst (**5**), that is already commercial, was developed by Grubbs et al in 2011. In scheme 2 it is possible to see that it can homodimerize olefins with excellent yield and very-high Z selectivity. Despite some small yields showed, the Z selectivity were greater than 80% in all of the reactions.⁶



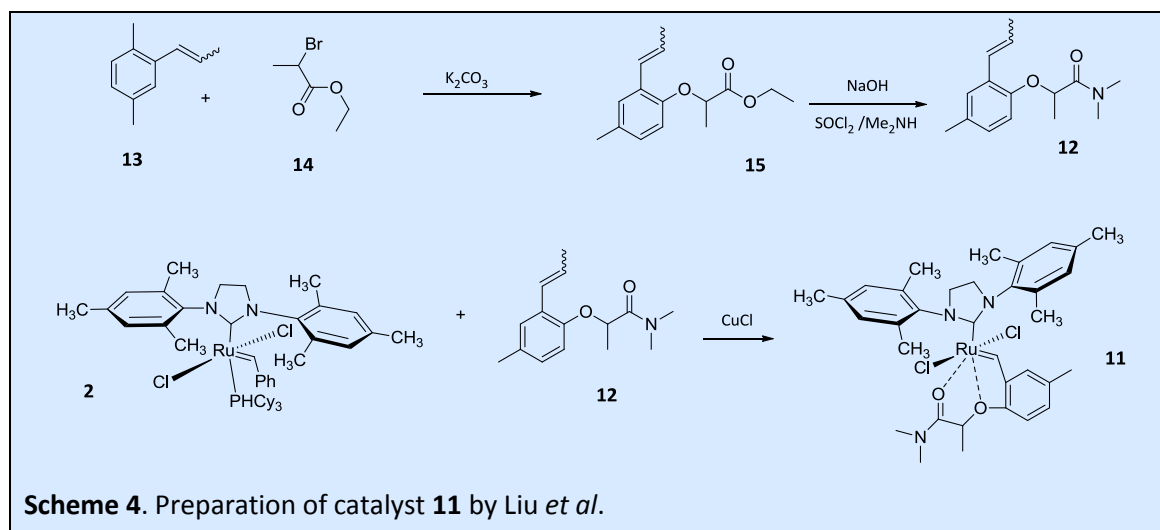
Also with the kinetic control as a target, the new ruthenium catalyst **6** was obtained by the reaction of the commercial catalyst **7** and the sodium salt (Z)-1,2-dicyanoethene-1,2-bis(thiolate)(**8**) in tetrahydrofuran at 22°C. This new catalyst was able to polymerize norbornene (**9**) with 92% yield and 98% of Z-selectivity in one hour.^{2,5}



Scheme 3. Synthesis of the ruthenium catalyst **6** from commercial catalyst **7**

Another challenge in cross-metathesis chemistry is the increase of the catalytic activity of a catalyst without losses in the stereoselectivity.⁵ Liu et al obtained a catalyst **11** that was an advance in this direction. It is easier to purify with silica gel column chromatography and it showed high stability in air, high yield in cross-metathesis reactions (94%) with initiation rate of catalyst higher than the Hoveyda catalyst.⁷

As shown in scheme **4**, they obtained the molecule **11** by the reaction of the commercial Grubs second generation catalyst (**2**) with the amide **12**. The amide **12** was obtained by reaction of 1,4-dimethyl-2-(prop-1-enyl)benzene (**13**) with ethyl 2-bromopropanoate (**14**) that results in the ester **15** and this is hydrolyzed, acylated and reacted with dimethylamine.



4. New challenges of ruthenium in olefins cross-metathesis catalysis

Despite the great advances obtained in recent years, there are still many challenges in the cross-metathesis reactions to be achieved. The development of reaction systems with no isomeric mixture formation is one of them. There is also the necessity of catalysts capable of catalyzing cross-metathesis reactions with α,β -unsaturated ketones, acids, esters and amides.

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