NHC Ligand Effects on Ru-Catalyzed Cross-Metathesis of Renewable Materials

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Abstract: As petrochemical resources become increasingly scarce and expensive, much attention has been focused on renewable resources from biomass as alternative options for producing basic building blocks for chemical manufacturing. Catalytic olefin metathesis represents a powerful tool to transform biosourced structural motifs in valuable commodity, fine, and specialty chemicals. In that respect, the appropriate choice of the catalyst is the key issue of each metathesis transformation. The current study examines the influence of different N-heterocyclic carbene (NHC) ligands containing one or two N-alkyl substituents on the efficiency of Hoveyda–Grubbs-type catalysts in the cross-metathesis reaction of ethyl oleate with cis-1,4-diacetoxy-2-butene and cross-metathesis of eugenol acetate with cis-1,4-dichloro-2-butene. Interestingly, the introduction of alkyl N-substituents in the NHC ligand was revealed as beneficial for catalytic performances in the examined cross-metathesis (CM) reactions, leading to higher activity and/or selectivity than those observed in the presence of the classical, commercially available Hoveyda–Grubbs second generation catalyst (HGII).

Keywords: cross-metathesis; renewable resources; NHC ligands; ruthenium catalysts; fatty acid esters; phenylpropenoids

1. Introduction

Olefin metathesis is a highly versatile method for the construction of new carbon–carbon double bonds, which finds important applications in the synthesis of pharmaceuticals, petrochemicals, polymers, and specialty chemicals [1–3].

In recent years, the gradual depletion of fossil resources and the strong need to limit the adverse environmental and health impacts of petroleum-based chemicals have pushed towards the use of renewable natural resources as green alternatives [4]. In the olefin metathesis field, readily available and inexpensive plant-derived molecules containing carbon–carbon double bonds are currently considered ideal raw materials to be employed for the synthesis of valuable compounds for the chemical industry [5–11]. Among all renewable raw materials, unsaturated fatty acid esters from vegetable oils, such as methyl or ethyl oleate, emerge as the most attractive chemical platforms for olefin metathesis. These compounds, in fact, can be easily transformed in a variety of high-value products via cross-metathesis (CM) with both unfunctionalized and functionalized olefins [12–23]. For instance, the CM of unsaturated fatty acid esters with various functional groups offers a versatile route for the synthesis of α,ω-difunctional compounds, which serve as chemical intermediates and polymer precursors.

Another class of renewable compounds that are particularly suitable for olefin metathesis transformations is represented by phenylpropenoids, such as safrole, eugenol, and estragole, typically found in essential oils. This class of compounds has been employed in CM reactions with different cross-partners to produce polyfunctional olefins, which can be successively transformed...
in many types of useful chemicals [24–30]. The increasing interest in metathesis applications involving molecules from renewable resources is strictly related to the development of highly efficient catalysts with improved functional group tolerance. The right choice of the catalyst is one of the key issues to render such processes attractive and viable for industrial use. In this view, easy-handling, stable olefin metathesis ruthenium-based catalysts coordinated with N-heterocyclic carbene (NHC) ligands are considered as good candidates for applications involving renewable feedstocks as substrates [21,25–29,31–33].

Recently, we have reported on Hoveyda–Grubbs-type catalysts bearing backbone-substituted symmetrical and unsymmetrical NHCs, characterized by at least one N-alkyl moiety. These complexes were found to be efficient catalysts for specific metathesis applications, proving to be in some cases more active and/or selective than the traditional, commercially available HGII (Figure 1) [34–39]. To get a deeper picture of the catalytic potential of this class of complexes and their applicability in the field of olefin metathesis with renewable chemicals, we herein describe two CM reactions, namely the CM of ethyl oleate with cis-1,4-diacetoxy-2-butene, and the CM of eugenol acetate with cis-1,4-dichloro-2-butene, promoted by \(\text{N,N' }-\text{ dialkyl (Ru1 and Ru2) and N-alkyl, N'-aryl (Ru3 and Ru4) NHC Ru-complexes depicted in Figure 1. N,N'-dialkyl complexes Ru1 and Ru2 differ from each other in the bulkiness of the alkyl substituent, whereas N-alkyl, N'-aryl Ru3 and Ru4 in that of the aryl substituent. The influence of the nature of N-substituents as well as of backbone configuration of NHC ligands in determining catalyst efficiency is therefore discussed.}

![Figure 1. The Hoveyda–Grubbs second generation catalysts used.](image)

2. Results and Discussion

2.1. Cross-Metathesis of Ethyl Oleate with Cis-1,4-Diacetoxy-2-Butene

The synthesis of Ru1–Ru4 was carried out as previously described [34,36,38]. In order to provide a comprehensive picture of the catalytic behavior of Ru1–Ru4, some key characterization data of these complexes are summarized in Table 1 [36,38]. In this table, the thermal stabilities displayed by Ru1–Ru4 are quantified as the percentage of undecomposed catalyst in \(\text{C}_6\text{D}_6\) after 1 day, 2 days, and 14 days at 60 °C under nitrogen; furthermore, the steric demand of the NHC ligands of Ru1–Ru4 is described by the percentage buried volume (% \(V_{\text{bar}}\)) [40,41], while their electron-donating properties by the Ru(II)/Ru(III) redox potentials [42]. As a general trend, catalysts possessing \(anti\)-related phenyl...
groups on the backbone turn out as more stable than the corresponding syn isomers and possess higher \( \%V_{\text{Bur}} \) values. Moreover, \( N,N' \)-dialkyl catalysts are found to be less stable than \( N \)-alkyl, \( N' \)-aryl complexes, with cyclohexyl substituted catalysts \( \text{Ru1-anti} \) and \( \text{Ru1-syn} \) emerging as the less stable and the less encumbered catalysts in the series.

**Table 1.** Percentage of undecomposed complex, \( \%V_{\text{Bur}} \) values, and redox potentials for Ru1–Ru4.

| Catalyst | %Catalyst Left (1 Day) | %Catalyst Left (2 Days) | %Catalyst Left (14 Days) | \( \%V_{\text{Bur}} \) | \( \Delta E_{1/2} \) (V) |
|----------|------------------------|-------------------------|--------------------------|-----------------|------------------|
| Ru1-anti | 98                     | 98                      | 25                       | 28.9            | 0.950            |
| Ru1-syn  | 79                     | 66                      | 21                       | 28.7            | 0.972            |
| Ru2-anti | 93                     | 92                      | 33                       | 31.0            | 1.00             |
| Ru2-syn  | 82                     | 73                      | 33                       | 30.9            | 0.996            |
| Ru3-anti | 100                    | 100                     | 42                       | 31.0            | 0.960            |
| Ru3-syn  | 82                     | 74                      | 32                       | 30.5            | 0.947            |
| Ru4-anti | 100                    | 100                     | 100                      | 31.8            | 0.950            |
| Ru4-syn  | 100                    | 100                     | 100                      | 31.5            | 0.961            |
| HGII     | 86                     | 84                      | 83                       | 32.9            | 0.860            |

1 For Ru1 and Ru2, see Reference [38]; for Ru3, Ru4, and HGII, see Reference [36].

Of note, both syn and anti isomers of \( \text{Ru4} \) displayed higher stability than commercial catalyst HGII, chosen as benchmark. All the NHC ligands of \( \text{Ru1–Ru4} \) display lower electron-donating properties than the symmetrical \( N,N' \)-diaryl NHC of HGII, as suggested by the higher values of the Ru(II)/Ru(III) redox potentials. This difference can be related to the presence of phenyl groups on the NHC backbone, regardless of their relative orientation. No other substantial effect can be appreciated, except that deriving from the presence of neopentyl \( N \)-substituents, which impart lower electron-donor abilities to the corresponding NHCs.

\( \text{Ru1–Ru4} \) were first tested in the CM of ethyl oleate (1) with cis-1,4-diacetoxy-2-butene (2) (Scheme 1).

**Scheme 1.** Cross-metathesis (CM) of ethyl oleate (1) with cis-1,4-diacetoxy-2-butene (2).

This CM transformation was chosen because it allows us to obtain valuable commodity chemicals from relatively inexpensive substrates. The desired cross-metathesis products, namely undecen-2-enyl
acetate (CM1) and ethyl 11-acetoxyundec-9-enoate (CM2), are both interesting substrates for several syntheses and for the preparation of short chain polymer precursors \[9,22,43\]. Moreover, undecen-2-yl acetate (CM1) can be transformed, under appropriate conditions, into polyallylic alcohols \[44\].

The CM reactions were conducted in toluene at 50 °C with a catalyst loading of 2.5 mol%. A fivefold excess of \(2\) is used to restrict the undesirable concurrent self-metathesis reaction of ethyl oleate leading to the secondary metathesis products octadec-9-ene (SM1) and diethyl octadec-9-enedioate (SM2).

The results are presented in Table 2. The ethyl oleate conversion, the reaction selectivity, and the yield of cross- and self-metathesis products were determined by gas chromatography (GC) with dodecane as an internal standard, wherein \(E\) and \(Z\) isomers were counted together. Each product was identified by gas chromatography-mass spectrometry (GC-MS) and its structure and configuration confirmed by \(^1\)H NMR spectroscopy.

| Entry | Catalyst \[mol\%\] | Conversion \[^2\] [%] | Selectivity \[^2\] [%] | Yield \[^2\] [%] |
|-------|---------------------|----------------------|----------------------|----------------|
|       |                     | CM1                  | CM2                  | SM1 | SM2 |
| 1     | Ru1-anti (2.5)      | 61                   | 87                   | 53  | 40  | 3  | 4  |
| 2     | Ru1-syn (2.5)       | 90                   | 96                   | 57  | 40  | 1  | 2  |
| 3     | Ru2-anti (2.5)      | 90                   | 92                   | 51  | 45  | 1  | 3  |
| 4     | Ru2-syn (2.5)       | -                    | -                    | -   | -   | -  | -  |
| 5     | Ru3-anti (2.5)      | 89                   | 95                   | 51  | 47  | 1  | 1  |
| 6     | Ru3-syn (2.5)       | -                    | -                    | -   | -   | -  | -  |
| 7     | Ru4-anti (2.5)      | -                    | -                    | -   | -   | -  | -  |
| 8     | Ru4-syn (2.5)       | -                    | -                    | -   | -   | -  | -  |
| 9     | HGII (2.5)          | 90                   | 94                   | 51  | 46  | 1  | 2  |
| 10    | Ru1-anti (1.0)      | -                    | -                    | -   | -   | -  | -  |
| 11    | Ru1-syn (1.0)       | 76                   | 94                   | 53  | 44  | 1  | 2  |
| 12    | Ru2-anti (1.0)      | 67                   | 90                   | 52  | 43  | 2  | 3  |
| 13    | Ru3-anti (1.0)      | 84                   | 94                   | 51  | 46  | 1  | 2  |
| 14    | HGII (1.0)          | 59                   | 89                   | 52  | 42  | 3  | 3  |

\(^1\) Reaction conditions: \[1\] = 0.14 M in toluene, 5 eq. \(2\), 50 °C, 12 h; \(^2\) determined by GC, using dodecane as an internal standard.

As can be seen from Table 2, very different results were registered. N,N′-dialkyl catalysts (entries 1–4) were found to be competent in this CM reaction, only Ru2-syn with neopentyl N-groups failed (entry 4), while N-alkyl, N′-aryl catalysts turned out to be practically inactive (entries 5–8), the only exception being Ru3-anti (entry 5). In all cases, yield of both desired cross-metathesis products, namely CM1 and CM2, was similar, and slightly better for CM1. Other products from side-reactions or double-bond isomerization were not observed. Even if the selected CM is a quite demanding reaction, we were quite surprised to find that it was prohibitive for complexes such as N-alkyl, N′-aryl catalysts Ru4-anti and Ru4-syn, that, on the contrary, were revealed as highly performing catalysts in the cross-metathesis of ethyl oleate with ethylene (ethenolysis) \[36\]. Interestingly, the presence of symmetrically substituted N-alkyl NHCs coordinated to the metal seems to favor the formation of more reactive catalytic species, especially when the alkyl group is a cyclohexyl (entries 1 and 2). In fact, in this case, both anti and syn isomers of Ru1 can promote the reaction, with the syn catalyst showing higher conversion than the anti congener (90% vs. 61%). It is also worth to note, that these two catalysts are the least bulky and stable in the series (see Table 1). The replacement of a cyclohexyl N-substituent in the NHC by the bulky mesityl group is deleterious for the catalytic activity of both anti and syn isomers of Ru4 (entries 7 and 8), which, by the way, are the most bulky and stable in the series (see Table 1). Except for Ru1-anti (entry 1), all the catalysts able to promote the reaction showed high conversions, comparable to those observed with commercial catalyst HGII (entry 9). Selectivity of the cross-metathesis reaction was in the range 87–96%. The best selectivity was observed when Ru1-syn was used (96%, entry 2). No trend in the electronic influence of the NHC ligand could be found.
Ru1, Ru2-anti, and Ru3-anti were then tested at lower catalyst loading (1.0 mol%, entries 10–14), as described by Behr [19] and Grela [21] for the CM of methyl oleate with 2. All the catalysts gave still satisfactory results in terms of conversion, with one exception, Ru1-anti, which was already less effective, and in these reaction conditions became inactive (entry 10). Notably, Ru1-syn, Ru2-anti, and Ru3-anti outperformed commercially available HGII, which showed a significant drop in conversion, from 90 to 59% (entry 14). As for selectivity, in all cases a similar level (around 90%) was maintained.

2.2. Cross-Metathesis of Eugenol Acetate with cis-1,4-Dichloro-2-Butene

The reactivity of the different catalysts was next studied in the CM of eugenol acetate (3) with cis-1,4-dichloro-2-butene (4) (Scheme 2). Eugenol acetate belongs to the family of phenylpropenoids, which are considered as important fine-chemical building blocks. It is one of the key constituents of clove essential oil, together with eugenol, from which it can be easily obtained by direct acetylation with acetic anhydride. It has been widely used as a food and flavor ingredient and has also been recognized for its antibacterial, antioxidant, and antivirulence activities. The CM of 3 with 4 affords the allylic chloride derivative CM3, which represents a useful intermediate for the synthesis of polymers and chemicals.

This transformation was carried out in CH2Cl2 at 40 °C using 2.5 mol% catalyst loading and 3 equivalents of 4 to minimize self-metathesis of 3. The catalytic performance of Ru1–Ru4 was compared to that of commercially available HGII and the results are summarized in Table 3.

![Scheme 2. CM of eugenol acetate (3) with cis-1,4-dichloro-2-butene (4).](image)

Table 3. CM of 3 with 4 in the presence of Ru1–Ru4 and HGII.

| Entry | Catalyst | Yield [%] | E:Z |
|-------|----------|----------|-----|
| 1     | Ru1-anti | 77       | 5.4 |
| 2     | Ru1-syn  | 84       | 5.4 |
| 3     | Ru2-anti | 70       | 3.2 |
| 4     | Ru2-syn  | 88       | 2.8 |
| 5     | Ru3-anti | 77       | 9.0 |
| 6     | Ru3-syn  | 60       | 2.0 |
| 7     | Ru4-anti | 75       | 7.0 |
| 8     | Ru4-syn  | 54       | 3.2 |
| 9     | HGII     | 50       | 7.4 |

1 Reaction conditions: [3] = 0.2 M in methylene chloride, 3 eq. 4, 40 °C, 12 h; 2 isolated yield; 3 E:Z ratios were determined by 1H NMR spectroscopy; 4 see ref. [38].

In all cases, no undesired side-products arising from self-metathesis and/or double bond migration reactions were observed. The only exception is the CM promoted by Ru3-syn, in which the formation of unidentified side-products was observed. All the eight catalysts were found to be more efficient than HGII, with Ru2-syn emerging as the most active among the examined catalysts. These results clearly indicate that the introduction of alkyl N-substituents is particularly advantageous for this CM reaction. As for the NHC backbone configuration, syn isomers of N,N’-dialkyl catalysts resulted as more active than their anti counterparts (entries 1–4), while the reverse behavior was observed in the group of N-alkyl, N’-aryl catalysts (entries 5–8). As for selectivity, no remarkable difference was noticed in the case of N,N’-dialkyl catalysts Ru1 and Ru2 (entries 1–4), for which both the isomers gave almost the same E/Z ratios and a slightly increased Z-selectivity was observed when N,N’-neopentyl catalysts...
Ru2 were used. On the contrary, in the case of Ru3 and Ru4, decorated with N-alkyl,N’-aryl NHC, differences in E/Z ratios were evident (entries 4–8). Anti isomers were indeed more selective than their syn congeners towards the formation of the desired CM product with a Z double bond. In general, as observed in the previous CM reaction, less stable catalysts with lower bulkiness of the NHC ligand turned out as the best performing catalysts. Unfortunately, no trend in the electronic influence of the NHC ligand could be established.

3. Materials and Methods

3.1. General Considerations

All reactions with Ru-based compounds were carried out under nitrogen using standard Schlenk and/or Glove-box techniques. Toluene and dichloromethane were purchased from Merck (Germany) and distilled before used. Ethyl oleate was purified through a column of neutral, activated alumina before use. All the other solvents and reagents were purchased from Merck or TCI Chemicals Europe (Belgium) and used as received. Catalysts Ru1–Ru4 were synthesized according to literature procedures [34,36,38].

GC analysis was performed on Agilent Technologies 7890 A instrument equipped with a HP5MSUI column (60 m 25 mm) using the following temperature program: 100 °C for 20 min, then 15°/min until 300 °C, and finally 300 °C for 8 min. The NMR spectra were recorded on BrukerAM 300 spectrometer (300 MHz for 1H; 75 MHz for 13C) or BrukerAVANCE 400 spectrometer (400 MHz for 1H; 100 MHz for 13C). The NMR samples were prepared dissolving about 10 mg of compound in 0.5 mL of the deuterated solvent.

3.2. Procedures for the CM of Ethyl oleate (1) and Cis-2,4-Diacetoxy-2-Butene (2)

Under a nitrogen atmosphere, 1 (75 µL) and dodecane (50 µL) were introduced. At this point, the t0 sample was prepared. After that, 2 (165 µL) was added and the mixture was transferred into a toluene solution of the catalyst (2.5 mol %). The reaction was placed in an oil bath at 50 °C for 14 h and then cooled in an ice bath and quenched with ethyl vinyl ether. After that, the GC sample was prepared in hexane. The samples were stored at −20 °C until GC analysis. For a representative chromatogram of the reaction mixture, see the supporting information (Figure S1).

The conversion was determined through comparison of the areas of 1 and of dodecane in the sample containing the aliquot of the crude reaction mixture (sample t) and in the a t0 sample using the following equation:

\[
\text{Conversion} \, (\%) = \left(1 - \frac{\text{Area} \, (1)_{t} \times \text{Area} \, (\text{dodecane})_{i0}}{\text{Area} \, (1)_{i0} \times \text{Area} \, (\text{dodecane})_{t}}\right) \times 100
\]

In order to calculate selectivity, response factors (rf) of all the components of the reaction mixture with respect to 1 (to which a rf = 1 was arbitrarily attributed) were determined. Starting from the areas in the chromatogram and the abovementioned rfs, selectivity and yield toward each (i) component were calculated as follows:

\[
\alpha \, (i) = \frac{\text{Area} \, (i)}{\text{rf} \, (i) \times \text{MW} \, (i)}
\]

\[
\text{Selectivity} \, (\%) = \frac{\alpha \, (\text{CM1}) + \alpha \, (\text{CM2})}{\alpha \, (\text{CM1}) + \alpha \, (\text{CM2}) + 2 \times [\alpha \, (\text{SM1}) + \alpha \, (\text{SM2})]} \times 100
\]

\[
\text{Selectivity} \, (i) \, (\%) = \frac{\alpha \, (i)}{\alpha \, (\text{CM1}) + \alpha \, (\text{CM2}) + 2 \times [\alpha \, (\text{SM1}) + \alpha \, (\text{SM2})]} \times 100
\]

\[
\text{Yield} \, (i) \, (\%) = \frac{\text{Selectivity} \, (i) \, (\%) \times \text{Conversion} \, (\%)}{100}
\]
3.3. Procedures for the CM of Eugenol Oleate (3) and Cis-1,4-Dichloro-2-Butene (2)

Under a nitrogen atmosphere, 47 µL of 3 and 77 µL of 4 were added simultaneously to a solution of the catalyst (2.5 mol%) in dry methylene chloride. The reaction mixture was refluxed under nitrogen overnight and then purified by column chromatography with hexane/ethyl acetate 9:1 as the eluent. The CM product (CM3) was obtained as a transparent oil. The E/Z ratios were determined by $^1$H NMR through integration of the methylene (CH$_2$-Cl) signals at δ 4.19 (Z) and δ 4.06 (E). For a representative $^1$H NMR spectrum, see the supporting information (Figure S2).

4. Conclusions

A series of ruthenium catalysts containing backbone-substituted symmetrical N,N′-dialkyl and unsymmetrical N-alkyl, N′-aryl NHC ligands were compared in two CM reactions of renewable substrates. Improved activities and selectivities, with respect to the commercially available HGII, were observed in both the reactions. Although the catalytic performances of the examined complexes are not easily rationalized in relation to the NHC ligand architecture, these results encourage further efforts towards the development of new catalysts containing N-alkyl substituents, since they seem to be suitable for several specific olefin metathesis applications, in which the general purpose NHC Ru catalysts are less competent.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/8/904/s1. Figure S1: Representative chromatogram of the crude reaction mixture from the CM of 1 and 2. Figure S2: Representative $^1$H NMR spectrum of the CM product (CM3) from reaction of 3 and 4 (CDCl$_3$, 400 MHz).

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