

Short communication

Improved reactivity in the conversion of nitrile-functionalized olefins by metathesis

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ARTICLE INFO

Article history:

Received 14 November 2015

Received in revised form 13 January 2016

Accepted 20 January 2016

Available online 21 January 2016

Keywords:

Methyl oleate
Cross-metathesis
Ruthenium
Acrylonitrile
Crotonitrile
FAME

ABSTRACT

In this contribution, we study the conversion of a bio-sourced unsaturated fatty ester by cross-metathesis with nitrile-functionalized olefinic partners (acrylonitrile and crotonitrile). A switch from terminal to internal olefins leads to higher conversion. This is in part rationalized by involvement of a more stable ruthenium ethylidene species with crotonitrile. A new carbenic complex forms upon reaction with the nitrile-functionalized olefins, that is also catalytically active.

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1. Introduction

In the view of dwindling fossil resources, the efficient use of bio-sourced, renewable materials as entries into valuable products is of prime importance. The family of fatty acid (or ester) derivatives, deriving from triglycerides extracted from plant oils, has attracted significant interest [1]. The crop selection can generate oils containing various unsaturated compounds, that can be transformed as fatty acid methyl esters (FAME). In order to functionalize those, olefin metathesis has been shown to be an utmost efficient tool [2]. Indeed, thanks to the spectacular development of ruthenium catalysts, this reaction has attained a high degree of maturity and combines high selectivity and productivity [3]. Cross-metathesis with functionalized olefins, such as methylacrylate has been developed and improved, affording reliable and efficient access to diesters amenable to application in polyester synthesis [4]. Moreover, it has also been shown that cross-metathesis of FAME or derivatives with acrylonitrile affords precursors to monomers for polyamide synthesis with high efficiency [5]. Recently, we have been able to show that switching from methyl acrylate to methyl crotonate has a significant positive impact on the conversion of FAME by cross-metathesis [6]. Thus, we proceeded to probe whether this beneficial effect could be encountered in the case of nitrile-substituted

reagents, namely by comparing the conversion of methyl oleate with acrylonitrile and crotonitrile.

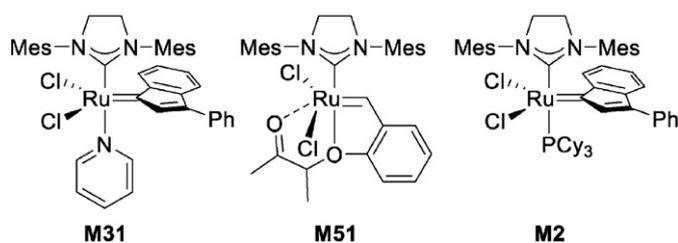
2. Experimental

All experimental operations were carried out under argon using Schlenk techniques or within a glove box. Commercial solvents were dried and deoxygenated by refluxing over appropriate drying agents under argon and distilled prior to use. Methyl oleate, acrylonitrile and crotonitrile were degassed and purified over activated alumina column (heated at 200 °C for 15 h under 10⁻⁵ mbar) shortly before use. Catalysts **M51**, **M31** and **M2** were supplied by Umicore. **G2** was purchased from Aldrich. Reaction mixtures were analyzed by GC using a Supelco SP-2380 column (60 m × 0.25 mm × 0.2 μm), argon as carrier gas, injector and detector temperature of 280 and 255 °C, respectively, heating program: 80 °C for 10 min, ramp of 20 °C/min up to 185 °C, hold for 5 min, ramp of 20 °C/min up to 250 °C, hold for 30 min. NMR spectra were recorded on Bruker Avance II 400 spectrometer equipped with a 5 mm TBI probe tuned at 400.3 MHz for ¹H, 100.7 MHz for ¹³C, and 162.1 for ³¹P. Standard experiments were run: 1D-¹H, 1D-¹H{³¹P} and 1D-³¹P{¹H} both with inverse gated decoupling, 1D-¹³C{¹H/³¹P}, 2D-[¹H-¹³C]-HSQC with gradients and sensitivity improvement. 1D-¹H and ¹³C chemical shifts were referenced to residual C₆D₅H peaks: 7.16 and 128.06 ppm, respectively (128.35 ppm for C₆D₅H in 2D-HSQC). Elemental analysis was performed on an Elementar VarioMicro in CHNS mode.

Abbreviations: TON, turnover number.

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Scheme 1. Catalysts used in this study (Mes: 2,4,6-Me₃-C₆H₂).

2.1. Typical metathesis run

A glass reactor equipped with a stirring bar was charged with the substrate (methyl oleate), 4 equiv. of cross-partner, 0.1 equiv. of tetradecane as internal standard and the solvent. Catalyst was added prior to closing the system, and the reaction mixture was heated at the indicated temperature. Samples were quenched by addition of few mL of O₂-saturated acetone and stored at –30 °C prior to analysis.

2.2. Synthesis of 7-CN

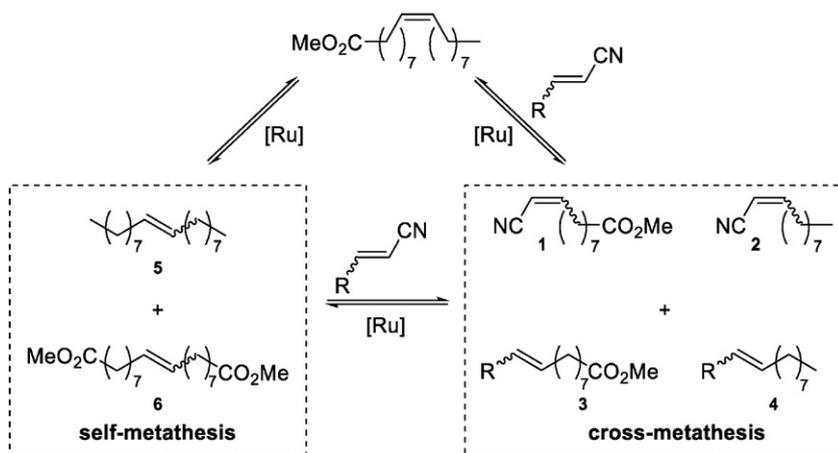
Grubbs second generation catalyst (100 mg, 0.118 mmol) and acrylonitrile (25 mg, 0.472 mmol) were stirred in toluene (5 mL) for 15 h at room temperature. After removal of volatiles by evacuation, the brown powder was washed with pentane (3 × 5 mL) and dried under vacuum, affording **7-CN** as a brown solid in a 80% yield. ¹H NMR (C₆D₆, 298 K): 18.46 (d, CHCN, ³J_{P-H} = 1.4 Hz, resolves as singlet upon ³¹P decoupling), 6.91 (s, 2H, C_{Ar}-H), 6.85 (s, 2H, 2H, C_{Ar}-H), 3.25 (s, 4H, NCH₂CH₂N), 2.67 (s, 6H, CH₃), 2.54 (s, 6H, CH₃), 2.44 (m, 3H, Cy), 2.19 (s, 3H, CH₃), 2.14 (s, 3H, CH₃), 1.82–0.85 (m, 30H, Cy); ¹³C{¹H} NMR (75.5 MHz, C₆D₆): 237 (Ru = C, detected via ¹H–¹³C HSQC, see Electronic Supporting Information), 217 (d, J_{PC} = 68 Hz, NCN), 139 to 131 (Mes, C_{arom}), 130.6 (Mes, *m*-CH), 130.1 (Mes, *m*-CH), 52 (NCH₂), 50.8 (NCH₂), 31.8 (d, J_{PC} = 18.2 Hz, Cy), 29.1 (Cy), 27.7 (d, J_{PC} = 10.7 Hz, Cy), 26.4 (Cy), 21.1 (Mes, *p*-CH₃), 20.9 (Mes, *p*-CH₃), 19.84 (Mes, *o*-CH₃), 18.85 (Mes, *o*-CH₃), ³¹P-{¹H} NMR (C₆D₆, 298 K): 33.3 ppm. IR: 2205 cm⁻¹, strong, with a shoulder at 2223 cm⁻¹ (ν_{CN}); Elemental analysis (C₄₁H₆₀Cl₂N₃PRu): Theor: C, 61.72; H, 7.58; N, 5.27; Found: C, 61.30; H, 7.86; N, 5.28.

3. Results and discussion

3.1. Cross-metathesis between methyl oleate and acrylonitrile

The conversion of unsaturated fatty esters was performed on the benchmark substrate methyl oleate. In a first step, we studied the conversion of methyl oleate by cross-metathesis with acrylonitrile catalyzed by third generation indenylidene and second generation Hoveyda–Grubbs-type catalysts (**M31** and **M51** [7], respectively, Scheme 1). Catalytic runs were carried out in batch mode, with no further addition of catalyst. Several products can be expected: As depicted on Scheme 2, cross-metathesis affords nitrile-functionalized (targeted) olefins **1** and **2**, along with olefinic compounds **3** and **4**. In addition, self-metathesis of methyl oleate yields **5** and **6**. Noteworthy, **3** and **4** can also react either by cross-metathesis with acrylonitrile to give **1** and **2**, or undergo self-metathesis to generate **5**, **6** and methyl oleate. Results are gathered in Table 1. Bruneau and coworkers reported that full conversion could be achieved with 2nd Hoveyda–Grubbs catalyst, affording **1** and **2** mostly as *cis* isomers (5%mol, 2 h, 100 °C in toluene) [5]. Only **2** and **3** (mostly *cis*) were formed.

Under these conditions, only moderate conversions were reached, with high selectivity toward cross-metathesis products. Under more forceful conditions, it was reported that reaction proceeds selectively to formation of **1** and **2** [5]. Higher temperatures are beneficial to the conversion, and to a lesser extent, to the selectivity in terms of cross- vs. self-metathesis. Interestingly, all cross-metathesis products are observed: even the terminal olefinic substrates are not fully converted. The relative proportions of vinyl- vs. nitrile terminated products (**1** and **2** vs. **3** and **4**) indicate that the former are converted into the latter, with release of ethylene. (or into the self-metathesis products **5** and **6**, though the selectivity toward self-metathesis remains low). In



Scheme 2. Methyl oleate self- and cross-metathesis with acrylonitrile (R = H) and crotonitrile (R = Me).

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