Research Article

Catalytic valorization of oil-derived fatty esters via cross-metathesis with nitriles

Pablo D. Nieres, Juan Zelin, Andrés F. Trasarti and Carlos R. Apesteguía

Catalysis Science and Engineering Research Group (GICIC), INCAPE, UNL-CONICET, Predio CCT Conicet, Santa Fe, Argentina

The cross-metathesis of methyl oleate with 3-pentenenitrile to obtain 2-undecene, methyl 9-undecenoate, methyl 11-cyano-9-undecenoate, and 3-dodecenenitrile was studied at 323 K in a batch reactor using second-generation Hoveyda–Grubbs (HG) catalysts. Self-metathesis of methyl oleate was the main undesired secondary reaction. For a 3-pentenenitrile/methyl oleate reactant ratio ($R_{3PN/MO}$) of one, the yield (η_{C-M}) and selectivity (S_{C-M}) to cross-metathesis products were 47 and 63%, respectively. The formation of cross-metathesis products increased with increasing 3-pentene initial concentrations, essentially because the reaction equilibrium was shifted to higher methyl oleate conversions. Thus, η_{C-M} and S_{C-M} were 74 and 83%, respectively, at $R_{3PN/MO} = 5$. Nevertheless, the HG complex was significantly deactivated when high $R_{3PN/MO}$ values were employed.

Practical applications : Metathesis reactions are becoming increasingly attractive in the oleochemistry industry because they offer novel routes for the valorisation of unsaturated fatty acid methyl esters (FAME) that are cheap feedstocks obtained by transesterification of natural oils and fats. Recently, the cross-metathesis of FAME with functionalized olefins such as esters, allylchlorides, and nitriles has been investigated to obtain renewable α,ω-bifunctional compounds. In particular, the cross metathesis of nitriles with FAME constitutes an attractive synthesis route toward the production of useful polyamide precursors from natural renewable resources. In this work we investigate the cross-metathesis of methyl oleate with 3-pentenenitrile, an internal unsaturated nitrile that does not contain conjugated C=C and C≡N bonds. The results presented in this work show that high yields (74%) and selectivities (88%) to cross-metathesis products are obtained using the second-generation Hoveyda–Grubbs Ru catalyst.

Keywords: 3-Pentenenitrile / Cross-metathesis / Hoveyda–Grubbs catalysts / Methyl oleate / Oleochemistry

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1 Introduction

The metathesis of unsaturated fatty acid methyl esters (FAME) to obtain value-added chemical and polymer intermediates is a field of increasing interest in green chemistry and oleochemistry [1–3]. Homogeneous catalysts have been successfully employed for converting unsaturated fatty acids and oils via metathesis reactions [4] although their performance may be limited by their tolerance towards the carboxylic acid or ester groups [5]. FAME metathesis has been studied using mainly Grubbs' Ru alkylidenes [6] and second generation Ru Hoveyda–Grubbs (HG) catalysts (Fig. 1) that are remarkably tolerant to the presence of moisture and oxygen [7, 8].

The cross-metathesis of FAME with simple non-functionalized alkenes like ethylene, 2-butene, and 1-hexene has been traditionally studied to produce less abundant medium-chain fatty acid esters that are valuable

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Correspondence: Prof. Carlos R. Apesteguía, Catalysis Science and Engineering Research Group (GICIC), INCAPE, UNL-CONICET, Predio CCT Conicet, Paraje El Pozo, (3000) Santa Fe, Argentina
E-mail: capesteg@fiq.unl.edu.ar
Fax: 54-342-4511170

Abbreviations: FAME, fatty acid methyl esters; **HG,** Hoveyda–Grubbs; **MO,** methyl oleate

Additional corresponding author: Prof. Andrés F. Trasarti,
E-mail: trasarti@fiq.unl.edu.ar

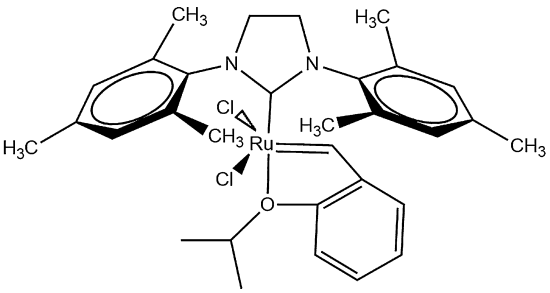
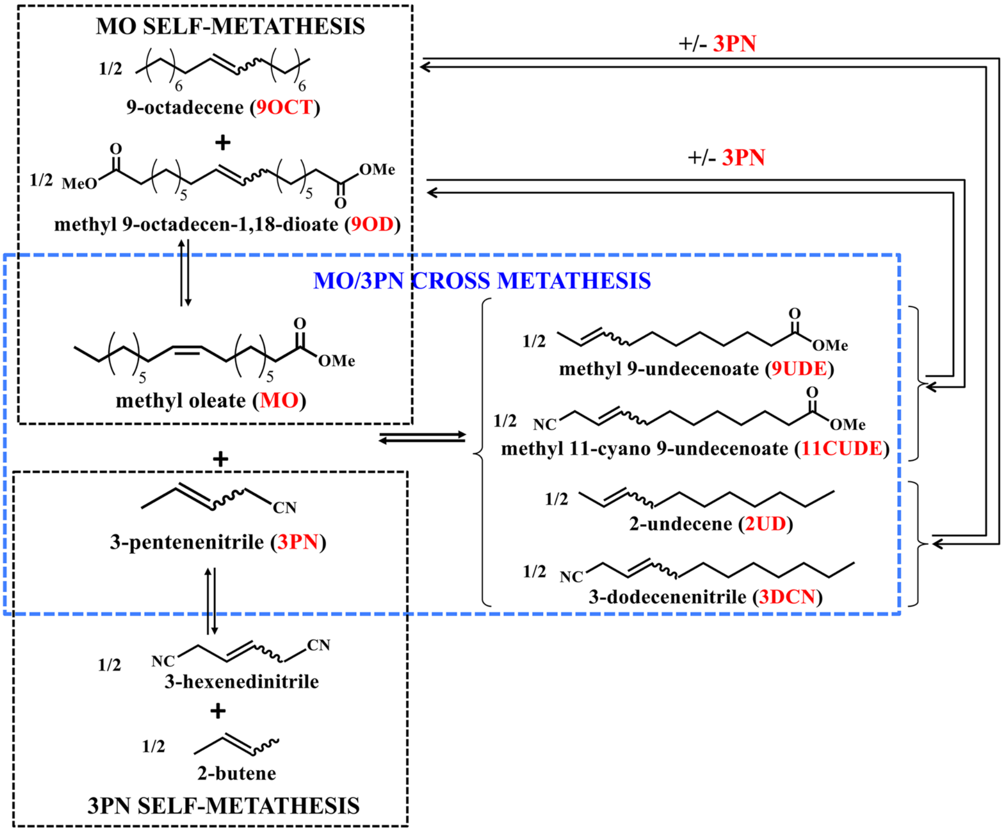


Figure 1. Second-generation Hoveyda–Grubbs catalyst.

intermediates in fine chemistry [9–11]. Recently, the cross-metathesis of unsaturated fatty acid methyl esters with functionalized olefins such as esters, allylchlorides, and nitriles has been investigated to obtain renewable α,ω-bifunctional compounds [12–15]. In particular, the cross metathesis of nitriles with oil-derived fatty acids or esters constitutes an attractive synthesis route toward the production of useful polyamide precursors from natural renewable resources. For example, Dixneuf et al. [16] investigated the synthesis of nylon 11 intermediates via the cross-metathesis of methyl 10-undecenoate, a castor oil-derived ester, with acrylonitrile, while Abel et al. [17] reported the production of nylons 12 and 13 precursors from the cross-metathesis of methyl oleate with allyl cyanide and 4-pentenenitrile, respectively. Acrylonitrile and allyl cyanides are terminal olefins that in cross-metathesis reactions form simultaneously ethylene, which is eliminated from the reaction mixture thereby shifting the metathesis equilibrium to the product formation. However, terminal olefins may deactivate Grubbs complexes because of the formation of unstable methylidene intermediates leading to hydride species that suppress the metathesis cycle [18, 19]. It is of practical and fundamental interest then to investigate the cross-metathesis of FAME with internal unsaturated nitriles that do not contain conjugated C=C and C≡N bonds. To the best of our knowledge, there are not previous reports on the cross-metathesis of FAME with this type of unsaturated nitriles.

Herein, we study the cross-metathesis of methyl oleate (MO) with 3-pentenenitrile (3PN) using the second generation Hoveyda–Grubbs Ru complex as homogeneous catalyst. The reaction forms 2-undecene (2UD), methyl 9-undecenoate (9UDE), methyl 11-cyano-9-undecenoate (11CUDE), and 3-dodecenenitrile (3DCN) as shown in Scheme 1. 3DCN is used to obtain dodecane nitrile, a saturated nitrile useful as a fragrance ingredient in the cosmetic, detergent, and cleaner industries [20]. 2UD is employed for the synthesis of a female sex pheromone of the



Scheme 1. Reaction network of the cross-metathesis of methyl oleate with 3-pentenenitrile.

raspberry cane midge [21]. The α,ω-bifunctional 11CUDE olefin is a valuable intermediate for 11-amino-9-undecenoic acid, a precursor of Nylon 12 [17]. Secondary reactions in the MO/3PN cross-metathesis reaction network are the self-metathesis of MO that produces 9-octadecene (9OCT) and dimethyl 9-octadecen-1,18-dioate (9OD), and the self-metathesis of 3PN yielding 3-hexenedinitrile and 2-butene. The products of MO self-metathesis, 9OCT and 9OD, may in turn react with 3PN to form the MO/3PN cross-metathesis products (Scheme 1). The results presented in this work show that high yields (74%) and selectivities (88%) to MO/3PN cross-metathesis products are obtained using the second-generation Ru Hoveyda–Grubbs (HG) catalyst when high 3PN/MO reactant ratios are employed.

2 Materials and methods

Second-generation Ru Hoveyda–Grubbs complex was obtained from Sigma–Aldrich (97%). The cross-metathesis of methyl oleate (Sigma–Aldrich, 99%) with 3-pentenenitrile (Sigma–Aldrich, 95%) was carried out in a Schlenk flask at 101.3 kPa and 293–323 K under Ar atmosphere. Toluene (Tedia, 99.5%) previously dehydrated with metallic Na and benzophenone under reflux was used as solvent. The reactor was loaded at room temperature under Ar with variable amounts of MO and 3PN together with toluene (10 mL) and n-dodecane (internal standard). Then the reaction mixture was stirred and heated to the reaction temperature in a thermostatic bath and the catalyst was added to start the reaction. Reaction products were analyzed by ex situ gas chromatography in an Agilent 6850 GC chromatograph equipped with a flame ionization detector and a HP-1 capillary column (50 m × 0.32 mm ID, 1.05 μm film). Samples from the reaction system were collected periodically for 60–300 min. Product identification was carried out by mass spectrometry using a Thermo Scientific ISQ Single Quadrupole spectrometer coupled with a Thermo Scientific Trace 1300 gas chromatograph equipped with a TR-5MS column (30 m × 0.25 mm × 0.25 μm film thickness). Besides the cross-metathesis reaction products (11CUDE, 9UDE, 2UD y 3DCN) it was detected the formation of 9OD and 9OCT from the self-metathesis of MO. Yields were calculated in carbon basis. The yield to MO/3PN cross-metathesis products (η_{C-M}, C atoms of cross-metathesis products formed/C atoms of MO fed) was determined as $\eta_{C-M} = \frac{\Sigma \alpha_i n_i}{\alpha_{\mathrm{MO}} n^0_{\mathrm{MO}}}$, where n_i are the moles of product i formed from the cross-metathesis reaction, α_i the number of C atoms in the product i molecule, n^0_{MO} the initial moles of MO, and α_{MO} the number of C atoms in the MO molecule. The yield to MO self-metathesis products was obtained as $\eta_{S-M} = \frac{\Sigma \alpha_j n_j}{\alpha_{\mathrm{MO}} n^0{}_{\mathrm{MO}}}$, where n_j are the moles of product j formed from the MO self-metathesis reaction and α_j number of C atoms in the product j molecule. The selectivity to cross-metathesis products was obtained as $S_{C-M} = \frac{\eta_{C-M}}{X_{\mathrm{MO}}}$, where X_{MO} is the conversion of MO; similarly the selectivity to the self-metathesis of MO was calculated as $S_{S-M} = \frac{\eta_{S-M}}{X_{\mathrm{MO}}}$.

The self-metathesis of MO and 3PN were carried out using the same reaction unit, analysis system and operation conditions than those described above for the cross-metathesis reaction.

3 Results and discussion

3.1 Self-metathesis of methyl oleate and 3-pentenenitrile

We initially investigated, the activity of HG complex for the self-metathesis of MO and 3PN because they are detrimental secondary reactions for the selective synthesis of MO/3PN cross-metathesis products (Scheme 1). In Fig. 2 we plotted the evolution of MO and 3PN conversions as a function of time. It is observed that X_{MO} rapidly reaches its equilibrium value of 50% [22], thereby showing that the HG complex efficiently promotes the self-metathesis of MO. From the slope at $t \to 0$ of the X_{MO} versus time curve in Fig. 2 we determined the initial MO conversion rate (r^0_{MO}, mol/h g_{HG}); we obtained a value of 1.13 mol/h g_{HG}. In contrast, we did not observe formation of any product from the self-metathesis of 3PN. Consistently, other authors have reported that the self-metathesis of unsaturated nitriles is hardly promoted by Grubb's Ru complexes, probably because of the cyano group capability for interacting with the coordination sphere of the Ru center, which hampers the complexation of the C=C bond required for the metathesis reaction [23–25].

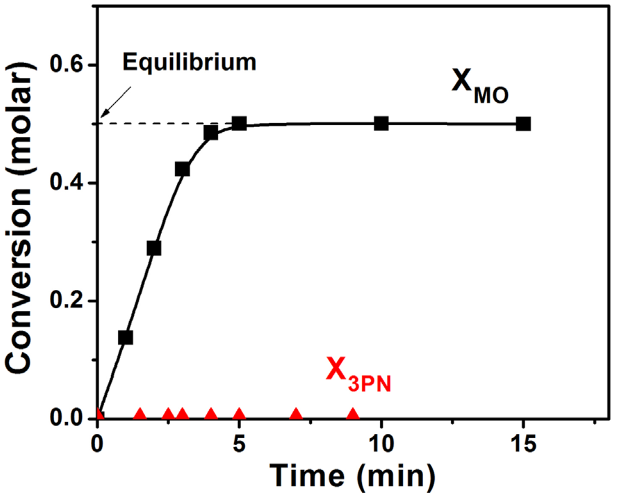


Figure 2. Self-metathesis of methyl oleate and 3-pentenenitrile [T = 323 K, $C^0_{3PN/MO}$/3PN = 0.0145 M, W_{HG} = 1.12 mg, HG/MO (3PN) and HG/3PN = 1.23 molar%, solvent: toluene, 10 mL].

3.2 Cross-metathesis of methyl oleate with 3-pentenenitrile

The activity and selectivity of HG complex for the MO/3PN cross-metathesis reaction were evaluated in standard catalytic runs of 300-min length. In Fig. 3A we plotted the curves of reactant conversions (X_{MO}, X_{3PN}) and yields to cross-metathesis (η_{C-M}) and MO self-metathesis (η_{S-M}) products as a function of time, obtained at 323 K and a reactant ratio ($R_{3PN/MO}$) of one. We did not observe any isomerization reactions and products were in accord with the olefin metathesis mechanism depicted in Scheme 1. Initially, MO was essentially converted to self-metathesis products 9OD and 9OCT; in fact, the initial MO conversion rate and the initial 9OD/9OCT formation rates determined from the X_{MO} versus t and η_{S-M} versus t curves of Fig. 3A, respectively, were practically the same ($r^0_{MO} = 1.11$ mol/h g_{HG}). This r^0_{MO} value is comparable to that determined above from Fig. 2 for the self-metathesis of MO. The initial 3PN conversion rate calculated from the corresponding curve in Fig. 3A was $r^0_{3PN} = 0.20$ mol/h g_{HG}. Figure 3B shows the product distribution evolution during the MO/3PN cross-metathesis reaction for $R_{3PN/MO} = 1$. 9OD and 9OCT were promptly formed at the beginning of the reaction and then went through a maximum at about 6 min reaction because they react with 3PN to form cross-metathesis products as depicted in Scheme 1. 9UDE, 11CUDE, 2UD, and 3DCN, the cross-metathesis products, continuously increased with reaction time up to reach equilibrium at the end of the 300-min run. Consistently with the results presented in Fig. 2, we did not detect the formation of 3PN self-metathesis products. The MO/3PN cross-metathesis is limited by equilibrium but we did not find values of equilibrium constant K for this reaction in the open literature. Thus, we determined here experimentally the K value by adding 1.2 mg of fresh HG complex at the end of the reaction to verify that the conversion and yield values in Fig. 3A after 300-min reaction were not modified by the catalyst addition and thereby confirming that the reaction system was in equilibrium. In this way, we verified that the MO equilibrium conversion (X^{Eq}_{MO}) for MO/3PN

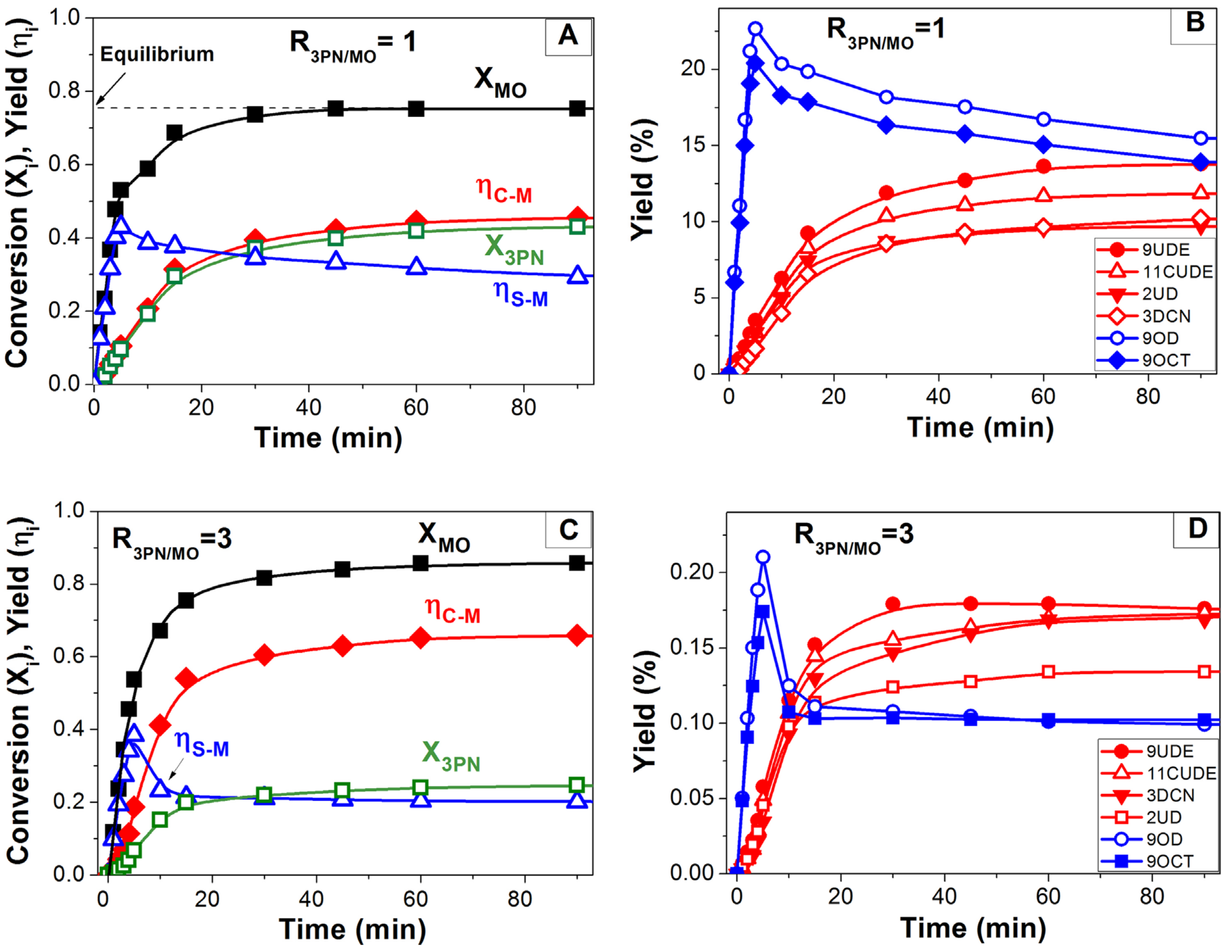


Figure 3. Cross-metathesis of MO with 3PN: Effect of the reactant ratio on catalyst activity and product distribution. (T = 323 K, C^0_{MO} = 0.0145 M, W_{HG} = 1.12 mg, HG/MO = 1.23 molar%, solvent: toluene, 10 mL).

Table 1. Cross-metathesis of methyl oleate with 3-pentenenitrile: Catalytic results

Reactant ratio	Initial 3PN concentration	Initial MO conversion rate	Initial turnover frequency	Conversion[a]		Equilibrium conversion		Yield[a]						Selectivity[a]		Carbon[a] balance
$R_{3PN/MO}$[b]	C^0_{3PN} (mol/L)	r^0_{MO} (mol/h g_{HG})	TOF (h^{-1})	X_{MO} (%)	X_{3PN} (%)	X^{EQ}_{MO} (%)	X^{EQ}_{3PN}	η_{2UD} (%)	η_{9UDE} (%)	η_{11CUDE} (%)	η_{3DCN} (%)	η_{C-M} (%)	η_{S-M} (%)	S_{C-M} (%)	S_{S-M} (%)	(% C)
1	0.0145	1.11	695	75	43	75	43	10	14	12	11	47	27	63	36	99
3	0.0435	0.96	595	86	23	86	23	13	18	17	17	65	20	76	23	99
5	0.0725	0.88	545	89	16	89	16	17	18	19	20	74	14	83	16	99
7	0.1015	0.82	514	81	10	93	12	19	18	18	16	71	10	88	12	100

$T = 323$ K, $C^0_{MO} = 0.0145$ M, $W_{HG} = 1.12$ mg, HG/MO $= 1.23$ molar%, solvent: toluene (10 mL).

[a] At the end of the 300-min catalytic runs.

[b] Molar ratio.

cross-metathesis at 323 K and $R_{3PN/MO} = 1$ is 75%. By employing $X^{Eq}_{MO} = 0.75$, we determined an equilibrium constant $K = 0.35$ that allowed us to calculate the X^{Eq}_{MO} values for other $R_{3PN/MO}$ ratios used in this work.

Results in Fig. 3A show that when the reaction system reached the equilibrium, the η_{C-M} and η_{S-M} values were 47 and 27%, respectively. In an attempt of improving the yield to cross-metathesis products, we performed additional catalytic tests at increasing $R_{3PN/MO}$ values, taking into account that the equilibrium of the MO/3PN cross-metathesis reaction is shifted to higher MO conversions when $R_{3PN/MO}$ is increased. In Fig. 3C and D we present the catalytic results obtained using $R_{3PN/MO} = 3$. Clearly, Fig. 3 shows that the formation of cross-metathesis products increased with $R_{3PN/MO}$ at the expense of MO self-metathesis products. Indeed, the η_{C-M} and η_{S-M} values for $R_{3PN/MO} = 3$ were 65 and 20%, respectively (Fig. 3C).

Quantitative results obtained at different reactant ratios are given in Table 1. Specifically, Table 1 presents the values of MO conversions, yields, selectivities, and carbon balances determined at the end of the runs for $R_{3PN/MO}$ reactant ratios of 1, 3, 5, and 7; initial MO conversion rates are also included. In all the cases, C^0_{MO} was 0.0145 mol/L. The initial MO conversion rate, r^0_{MO}, decreased with $R_{3PN/MO}$, from 1.11 mol/h g_{HG} ($R_{3PN/MO} = 1$) to 0.82 mol/h g_{HG} ($R_{3PN/MO} = 7$) thereby suggesting that the reaction is negative order in 3PN. We also included in Table 1 the values of the initial turnover frequency (TOF, mol MO converted/mol HG × h); similarly to the observed r^0_{MO} versus $R_{3PN/MO}$ trend, TOF decreased from 695 to 514 h^{-1} when $R_{3PN/MO} = 1$ was increased from one to seven.

On the other hand, X^{Eq}_{MO} increases from 75% at $R_{3PN/MO} = 1$ to 93% at $R_{3PN/MO} = 7$; the MO conversions determined at the end of our catalytic runs reached the X^{eq}_{MO} values for $R_{3PN/MO}$ between one and five. Nevertheless, X_{MO} was only 81% at $R_{3PN/MO} = 7$, significantly lower than the corresponding X^{Eq}_{MO} value (93%), which shows that the MO/3PN cross-metathesis reaction is inhibited at high 3PN concentrations. η_{C-M} increased from 47% ($R_{3PN/MO} = 1$) to 71% ($R_{3PN/MO} = 7$) at the expense of η_{S-M}; consistently, the selectivity to cross-metathesis products, S_{C-M}, increased from 63 to 88% when $R_{3PN/MO}$ was varied from one to seven. It is worth noting that the cross-metathesis product distribution did not change significantly with $R_{3PN/MO}$. Finally, the last column in Table 1 shows that the carbon balance was close to 100% in all the cases, which indicates that HG catalysts are highly selective for the formation of self- and cross-metathesis products.

In order to get more insight on the reaction kinetics and mechanism an additional catalytic test was carried out using $R_{3PN/MO} = 5$ (Fig. 4). The reactor was initially fed only with MO and the self-metathesis reaction proceeded reaching equilibrium; then, 3PN was added to the reactor and the evolution of the products of the cross-metathesis

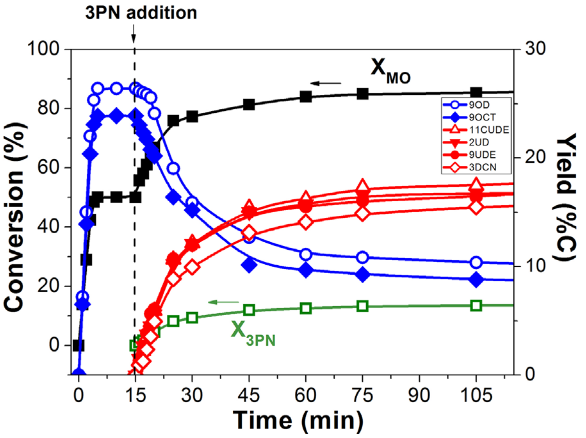


Figure 4. Addition of 3PN following the equilibrium of the MO self-metathesis reaction. [$T = 323$ K, $C^0_{MO} = 0.0145$ M, $C^0_{3PN} = 0.0725$ M $W_{HG} = 1.12$ mg, HG/MO = 1.23 molar%, solvent: toluene, 10 mL].

of 3PN with MO, 9OCT, and 9OD was followed as a function of time, as shown in Fig. 4. From the curves of Fig. 4 we determined the initial reactant conversion rates following the addition of 3PN and obtained: $r^0_{3PN} = 0.35$ mol/h g_{HG}, $r^0_{MO} = 0.25$ mol/h g_{HG}, $r^0_{9OCT} = 0.07$ mol/h g_{HG}, $r^0_{9OD} = 0.06$ mol/h g_{HG}. Overall, we observe that the 3PN consumption rate is similar to the sum of MO, 9OCT, and 9OD conversion rates, which is consistent with the reaction pathways shown in Fig. 1. We also determined the total initial formation rate of cross-metathesis products and obtained $r^0_{C-M} = 0.71$ mol/h g_{HG} that corresponds approximately to $2\ r^0_{3PN}$, as predicted by the reaction network in Scheme 1. From all these data, and the r^0_{MO} value determined when co-feeding MO and 3PN at $R_{3PN/MO} = 5$ ($r^0_{MO} = 0.88$ mol/h g_{HG}, Table 1) we infer that the MO/3PN reaction mechanism involves initially the rapid MO conversion via MO self-metathesis, followed then by the cross-metathesis of MO, 9OD, and 9OCT with 3PN.

Finally, we explored in more details the inhibiting effect of 3PN for the MO/3PN cross-metathesis reaction promoted by second-generation Hoveyda–Grubbs complexes.

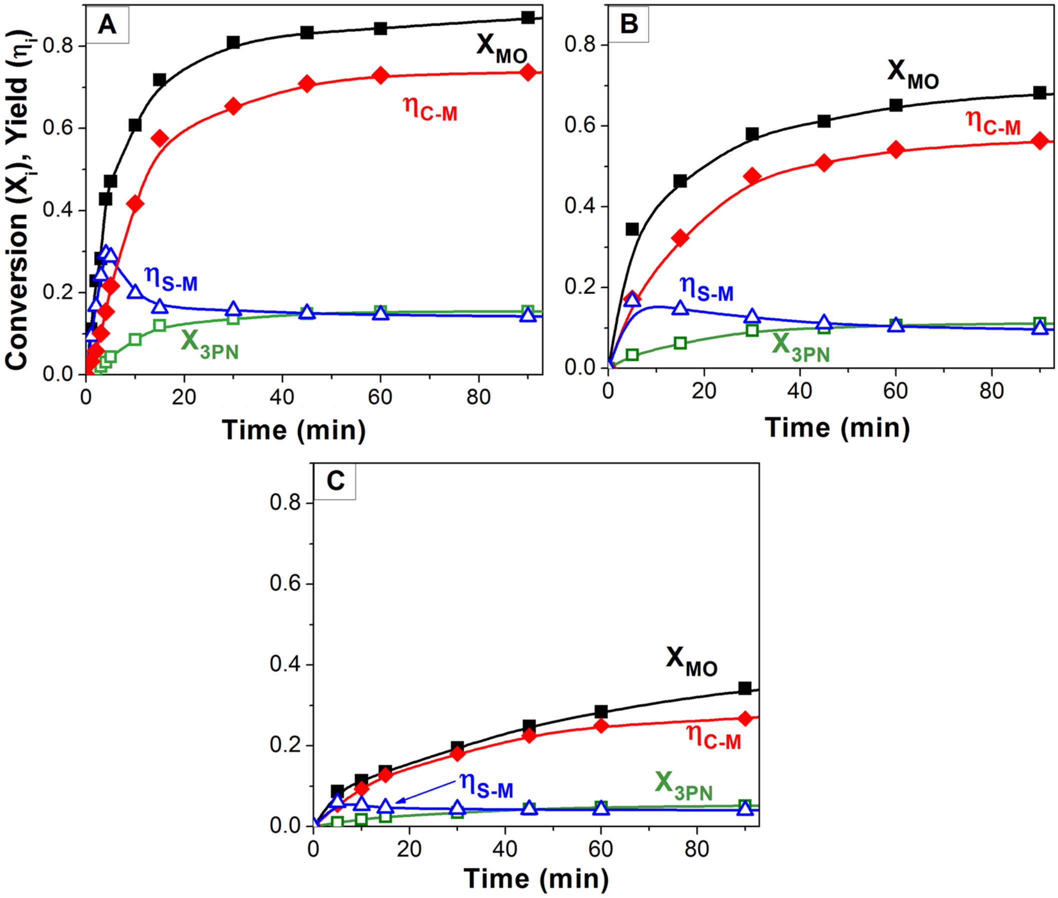


Figure 5. Cross-metathesis of MO with 3PN: Effect of contacting the HG complex with 3PN before the addition of MO. Contact times: 0 min (A), 30 min (B), 60 min (C). [$T = 323$ K, $C^0_{MO} = 0.0145$ M, $C^0_{3PN} = 0.0725$ M, $W_{HG} = 1.12$ mg, HG/MO = (1.23 molar%), solvent: toluene, 10 mL].

Specifically, 3PN and HG complex were contacted for increasing times before adding methyl oleate to start the cross-metathesis reactions. Figure 5 shows the catalytic results obtained after contacting 3PN and HG for 0, 30, and 60 min before the addition of MO. Clearly, X_{MO} and X_{3PN} as well as η_{C-M} and η_{S-M} diminished as the contact period between 3PN and HG was increased, thereby confirming that the 3PN/HG interaction may inhibit the ability of the Ru complex for promoting metathesis reactions.

4 Conclusions

The cross-metathesis of methyl oleate with 3-pentenenitrile is efficiently promoted by the second-generation Hoveyda–Grubbs catalyst. Selective formation of cross-metathesis products (2-undecene, methyl 9-undecenoate, methyl 11-cyano-9-undecenoate, and 3-dodecenenitrile) greatly depends on the 3-pentenenitrile/methyl oleate reactant ratio. The increase of $R_{3PN/MO}$ ratio shifts the equilibrium to high MO conversions and suppresses the MO self-metathesis competitive reaction. In this work, we report that the yield and selectivity to MO/3PN cross-metathesis products are 47 and 63%, respectively, for $R_{3PN/MO} = 1$ and increase to 74 and 83% for $R_{3PN/MO} = 5$. Nevertheless, deactivation of HG catalysts increases with 3-pentenenitrile concentration and the cross-metathesis reaction is markedly inhibited for 3PN/MO reactant ratios higher than 5.

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The authors have declared no conflict of interest.

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