DOI: 10.1002/cssc.201200086

Tandem Catalytic Acrylonitrile Cross-Metathesis and Hydrogenation of Nitriles with Ruthenium Catalysts: Direct Access to Linear α, ω -Aminoesters from Renewables

Xiaowei Miao,^[a] Cédric Fischmeister,^[a] Christian Bruneau,^{*[a]} Pierre H. Dixneuf,^{*[a]} Jean-Luc Dubois,^[b] and Jean-Luc Couturier^[b]

Dedicated to Prof. Hubert Le Bozec, a pioneer in the field of metal complexes for nonlinear optics, on the occasion of his 60th birthday.

The development of single catalyst precursors capable of performing multiple, mechanistically distinct reactions to reach complex molecular architectures as well as useful industrial chemicals and materials using more straightforward methods is a challenge.^[1] Such developments require the discovery of catalyst systems that can be applied to a useful catalytic transformation of industrial importance. Such catalysts also contribute to the creation of economical processes with greener aspects, and have the potential to achieve more efficient transformations of renewables. The objective of our work is to present the production of α , ω -amino esters, precursors of polyamides, from renewable plant oil derivatives by using a catalytic system that is able to perform two consecutive catalytic reactions.

Polyamides occur in nature as proteins, leading to wool and silk, but are especially the basis of thermohardening resins and synthetic fibers with many applications, for example in sport equipment.^[2] Industrially they are commonly synthesized from monomers derived from petroleum products, such as diamines, diacids, and aminoacids.^[3] This increasing interest in polyamides has recently motivated the search for processes offering, at least, a partial new supply to polyamide precursors from renewable resources,^[4] rather than from fossil sources. Recently, a first step in this direction has been made by crossmetathesis transformations of unsaturated acid derivatives arising from plant oils with functional olefins^[5] into bifunctional fatty esters, including α, ω -nitrile esters.^[6] However, the hydrogenation of the nitrile functionality associated to metathesis remains a challenge for the production of amines, as the nitrile hydrogenation in industry is mainly performed with heterogeneous reducing catalysts such as Raney cobalt or nickel,^[7] but usually with moderate selectivity.^[8]

The catalytic homogeneous hydrogenation of nitriles represents a potentially valuable route to primary amines. However, it requires drastic conditions and brings difficulty in isolating the target compounds due to side products consisting mainly

[a] Dr. X. Miao, Dr. C. Fischmeister, Dr. C. Bruneau, Prof. P. H. D	ixneuf
Organométalliques: Matérieux et Catalyse	
Institut Sciences Chimiques de Rennes	
UMR 6226 CNRS-Université de Rennes	
Campus de Beaulieu, 35042 Rennes (France)	
[b] Dr. JL. Dubois, Dr. JL. Couturier	
ARKEMA, CRRA,	

BP 63 Rue Henri Moissan, 69493, Pierre Bénite (France)

Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.201200086.

of secondary and tertiary amines,^[9] but it has not been strongly investigated until now. Only a few examples have shown to be very selective in producing the primary amines.^[9a, 10, 11, 12] Whereas rhenium-nitrosyl catalysts favor hydrogenation of nitriles into secondary amines,^[9c] Hidai and co-workers have reported improvements in the efficiency and selectivity for the hydrogenation of benzonitrile to benzylamine by addition of catalytic amounts of alkoxide base to a ruthenium amido complex at 80 °C and 30 bar of H₂.^[10b] Morris^[11a] has applied a ruthenium hydride complex [Ru(H)(Cl){PPh₂[(ortho-C₆H₄)CH₂NHCH₂-]}2] with tBuOK that promotes the selective catalytic nitrile hydrogenation of benzonitrile at 20 °C under 14 bar of H₂. Leitner and co-workers, using a pincer ruthenium-hydride catalyst, have shown that high selectivity in primary amines could be obtained, especially with water added to toluene, under 75 bar H₂ at 135 °C for 24–45 h,^[10c] and Sabo-Etienne et al. have hydrogenated benzonitrile into benzylamine under mild conditions (RT, 3 bar H₂, 2-24 h) using [RuH₂(H₂){P(cyclopentyl)₃}₂] catalyst.^[11b] It is noteworthy that the latter catalysts operate without base additives. Recently, Beller et al.^[12] have reported that a commercially available ruthenium complex $[Ru(cod)(methylallyl)_2]$ (cod = 1,5-cyclooctadiene) catalyzed the hydrogenation of various nitriles in the presence of both a phosphine ligand and tBuOK at 80-140 °C and 50 bar of H₂ to afford the corresponding amines with good to excellent yields.^[12b] They have also shown that milder conditions could be obtained through replacement of phosphine ligands by Nheterocyclic carbenes.^[12c] They demonstrated that the addition of NH₄Cl increases the selectivity towards the production of primary amines by inhibiting their further transformation into secondary amines. For unsaturated fatty nitriles, for example, that of beef tallow derivatives, hydrogenation into amines has been performed with a carbon-modified nickel catalyst to retain double bonds.^[7g]

Recently, we have reported a tandem ruthenium-catalyzed cross-metathesis (CM) hydrogenation of unsaturated esters derived from plant oil derivatives, which provided saturated nitrile-acid and ester compounds,^[6a] thus retaining the non-hydrogenated nitrile functionality. In this work it was shown that following the cross-metathesis step, the ruthenium alkylidene metathesis catalyst was totally consumed and that the residual ruthenium species was still an efficient hydrogenation catalyst. Whereas the cross-metathesis conditions of long-chain alkenes with acrylonitrile have been discovered,^[6] the consecutive catalytic hydrogenation into amines has not been investigated.

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

WILEY ONLINE LIBRARY

1

IEMSUSCHEM



Scheme 1. Tandem cross-metathesis and hydrogenation to produce linear α,ω -amino acids/esters.

We now report for the first time that following the ruthenium-alkylidene-catalyzed cross-metathesis of alkenes with acrylonitrile (Scheme 1, step a) the residual ruthenium species can be used for the direct catalytic hydrogenation of the formed nitriles with high selectivity into primary amines (step b), and that the tandem catalytic cross-metathesis-hydrogenation reactions of unsaturated fatty esters compounds allow the direct formation of α, ω -linear aminoester monomers. The latter are precursors for the production of polyamides from renewable resources.^[13]

Our initial studies were carried out with methyl undec-10enoate 1 derived from castor oil^[14] with 2 equivalents of acrylonitrile using 3 mol% of Grubbs-Hoveyda 2nd generation catalyst I in toluene (Scheme 2).



Scheme 2. Ruthenium-alkylidene olefin metathesis catalysts evaluated for acrylonitrile cross-metathesis and subsequent hydrogenation.



formed in moderate yield (entries 2, 3). Thus, besides the addition of tBuOK, the influence of some other additives, such as bidentate phosphorus-containing ligands, ammonium chloride or co-solvents, was then examined (entries 4-9). The conversion of 2 into 4 was decreased by each additive and all tests led to lower yields of the target product 4. More specifically, the addition of 1,2-bis(diphenylphosphino)ethane even inhibited the hydrogenation step from 2 into 3 (entry 4). Ammonium chloride, usually used to pre-

vent secondary amines formation,^[8c, 10b, 12] actually decreased the selectivity into long-chain primary amine as only 64% of monoalkylamine 4 was obtained (entry 6). Transesterification of 3 occurred in the reaction with *i*PrOH applied as co-solvent (entry 9).

The amount of tBuOK and hydrogenation time for selective conversion were also investigated (Table 1, entries 10-14). Increasing the amount of base up to 30 mol% with 20 bar of initial hydrogen pressure led to 92% yield of 4 (entry 11). At higher base concentrations, a slight decrease in activity was observed (entry 12). With shorter reaction times of 16-24 h, the conversion of 3 into 4 was observed in lower yield (entries 13-14). A metal-free blank hydrogenation test was performed on isolated 2 in toluene at 80 °C under 30 bar of H₂ in the presence of 30 mol% of tBuOK. After 48 h, no conversion could be detected, thus confirming the involvement of the residual ruthenium species in the nitrile reduction step. Notably, with the most efficient conditions (entry 11), whereas primary alkylamines formation usually leads to secondary and even tertiary alkylamine by-products, only the primary amine 4 was formed with this catalyst system without the requirement for addition of NH₄Cl.

Having demonstrated the best result obtained by using Grubbs-Hoveyda catalyst I for the cross-metathesis step and the hydrogenation step promoted by the ruthenium catalyst

Following the cross-metathesis reaction performed at 100°C for 1 h, the crude reaction mixture containing the ruthenium catalyst was transferred into an autoclave and charged with H₂. The results are shown in Table 1. The first attempt was run without any additive at 80°C with 30 bar of H₂ for 48 h. Notably, no aminoester was observed, methyl 11-cyanoundecabut noate (3) was isolated as the sole product (Scheme 3); Table 1, entry 1]. To access the formation of aminoester, the influence of the addition of potassium tert-butoxide to the catalyst was investigated. Indeed, in the presence of tBuOK, methyl 12-aminododecanoate (4) was

2

Table 1. Influence of additives on the hydrogenation step. ^[a]									
Entry	tBuOK [mol%]	Additive	Amount [mol%]	H ₂ [bar]	t [h]	2	GC yield (isolated yield 3) [%] 4	
1	_	_	_	30	48	_	93 (90)	_	
2	15	-	-	30	48	-	10	79 (65)	
3	15	-	-	20	48	-	15 (10)	74 (60)	
4	15	dppe ^[b]	6 mol %	20	44	71	23	-	
5	15	dppb ^[c]	6 mol %	20	44	-	86	5	
6	15	NH₄CI	10 mol%	20	48	-	8	64	
7	15	MeOH	5 mL	20	44	-	33	31	
8	30	DMC ^[d]	5 mL	20	44	-	93	-	
9	30	<i>i</i> PrOH	5 mL	20	44	-	80 ^[e]	8	
10	10	-	-	20	48	-	22	65	
11	30	-	-	20	44	-	-	92 (85)	
12	60	-	-	20	48	-	-	88	
13	30	-	-	20	16	-	67	25	
14	30	-	-	20	24	-	44	45	
[a] Reaction conditions: 0.5 mmol of 1, 1 mmol of acrylonitrile, 0.015 mmol of Grubbs-Hoveyda 2 nd generation									

(I), 10 mL of toluene for 1st step; 20–30 bar H₂, 80 °C, 15–60 mol% of tBuOK for the 2nd step. [b] dppe = Ph₂PCH₂CH₂PPh₂. [c] dppb=Ph₂P(CH₂)₄PPh₂. [d] DMC=dimethyl carbonate). [e] Isopropyl nitrile ester was isolated instead of 3.

www.chemsuschem.org © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim **F** These are not the final page numbers!

with



Scheme 3. Tandem catalytic ester 1/acrylonitrile cross-metathesis and hydrogenation.

residue in the presence of 30 mol% of tBuOK, 20 bar of H₂ (Table 1, entry 11), we examined the influence of different bases on the yield of aminoester under the same reaction conditions (Table 2, entries 1-5). The reaction with addition of po-

Table 2. Influence of base nature and initial olefin metathesis catalystprecursor on the production of aminoester $4_{i}^{[a]}$								
Entry	Catalyst precursor	Base	Amount [mol%]	t [h]	GC yield [%] 3			
1	I	КОН	60	67	-			
2	I	КОН	30	74	40			
3	I	NaOH	60	67	-			
4	I	Cs ₂ CO ₃	30	67	10			
5	I	LDA	30	74	82			
6	II	-	-	48	93			
7	II	<i>t</i> BuOK	15	45	-			
8	П	<i>t</i> BuOK	40	45	72			
9	III	<i>t</i> BuOK	15	48	74			
10	III	<i>t</i> BuOK	40	48	48			
[a] Reaction conditions: 0.5 mmol of 1, 1 mmol of acrylonitrile,								
0.015 mmol of ruthenium catalyst, 10 mL of toluene for the 1 st step;								
20 bar H_2 , 80 °C, 44–67 h for the 2 nd step.								

tassium hydroxide, sodium hydroxide, or cesium carbonate afforded good to excellent yields of 4 (entries 1-4). However, the reaction with lithium diisopropylamide, a stronger base than tBuOK, afforded the saturated nitrile-ester compound 3 as the major product (entry 5). The reaction with 60 mol% of KOH provided 90% yield, whereas with only 30 mol% of KOH, 56% yield of 4 was obtained together with 40% yield of 3 (entries 1-2). The influence of the nature of the initial alkene metathesis ruthenium catalyst was also of interest to investi-

gate (entries 6-10). The tandem cross-metathesis and hydrogenation with the new ruthenium complex II, the so-called Umicore M51, provided similar results to the Grubbs-Hoveyda complex I but with the advantage of requiring only 15 mol% of tBuOK (entry 7), instead of 30 mol% in the case with I (Table 1, entry 11). Increasing the base concentration gave a decrease of the yield of 4 (Table 2,

entry 8). The reaction Grubbs 2nd generation catalyst III neither offered a high yield of 2 at the cross-metathesis step (74% guantitatively transformed into 3) nor good selectivity to aminoester in the sequential hy-4 drogenation step (entries 9, 10).

tion with 1 mol% instead of 3 mol% of I yielded only 10% of aminoester 4, and 3 was obtained as major product; however, no other byproduct was observed. It is noteworthy that without the use of the base in the second step, the hydrogenation of the C=C bond is selective whereas the presence of a coordinating base further favors reduction of the nitrile into amine.

The influence of the initial catalyst loading was vital, the reac-

Another possible approach to C_{12} α, ω -nitrile-ester 3 and then α,ω -aminoester 4 would involve the tandem cross-metathesis with methyl acrylate of undec-10-enenitrile 5, readily obtained from ammoniation of undecylenic acid,^[15] and then the sequential catalytic hydrogenation of the nitrile-ester intermediate 6 with the ruthenium catalyst residue (Scheme 4). Thus, the reaction of 5 with 2 equiv methyl acrylate was performed in toluene for 1 h at 100 °C using 3 mol% of ruthenium catalyst I. The reaction led to complete transformation of 5 into the two stereoisomers of 6. Then the reaction mixture was transferred into an autoclave charged with 30 mol% of tBuOK, 20 bar of H₂, and stirred at 80 °C for 40 h. The target aminoester 4 was obtained in 96% GC yield. The conversion into 4 decreased to 50% when a lower amount of tBuOK (15 mol%) was added for the sequential hydrogenation step. The initial catalyst loading of 3 mol% was again crucial as, with an initial loading of 1 mol%, no conversion into 4 was observed.

We found that the cross-metathesis of 5 with methyl acrylate into unsaturated nitrile-ester 6 could proceed at room temperature with excellent yield (>98%),^[6c] thus the catalytic hydrogenation activity of the ruthenium residue arising from the cross-metathesis step under milder conditions was investigated. The reaction of 5 with methyl acrylate using 3 mol% of catalyst I was carried out in toluene for 1 h at room temperature. Then the reaction mixture was transferred into an autoclave charged with 30 mol% of tBuOK, 20 bar of H₂, stirred at 80 °C for 40 h. As expected, the aminoester 4 was obtained in



Scheme 4. Tandem catalytic nitrile 5/methyl acrylate cross-metathesis and hydrogenation.

ChemSusChem 0000, 00, 1-5

3 www.chemsuschem.org © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim These are not the final page numbers! **77**

CHEMSUSCHEM





Scheme 5. Sequential catalytic synthesis of aminoester 10 from diester 7.

97% GC and 90% isolated yields. The catalytic amount of tBuOK in this case could be decreased to 20 mol%, and the hydrogenation of both C=C and CN groups still remained highly efficient (95% GC yield).

The comparison of tandem cross-metathesis/hydrogenation of both renewable unsaturated ester 1 (Scheme 3) and nitrile 5 (Scheme 4) shows that they are very competitive to reach the same C₁₂ aminoester via these catalytic tandem reactions.

The tandem catalytic reactions, cross-metathesis with acrylonitrile/hydrogenation, were then applied to the renewable fatty compound **7** as an attempt to produce the $C_{11} \alpha, \omega$ -aminoester 10 (Scheme 5). The reaction of (Z)-dimethyl octadec-9enedioate 7, obtained via bioconversion of sunflower $oil^{[16]}$ or self-metathesis of oleic acid derivatives,^[17] with 4 equivalents of acrylonitrile was performed in toluene for 2 h and using 6 mol% of catalyst I, considering the relative catalyst precursor loading for the formation of two molecules of unsaturated nitrile-ester 8 from 7. Then the reaction mixture was transferred into an autoclave charged with 60 mol% of tBuOK, 20-30 bar of $H_{2\prime}$ and stirred at 80 °C for 48 h (Scheme 5). C_{11} aminoester monomer 10 was obtained in 89% GC yield (78% isolated yield) from the reaction with 30 bar of H₂. A decrease of initial catalyst I loading to 3 mol% led only to 25% of isolated yield of 10 and 47% of saturated nitrile-ester compound 9.

In summary, selective catalytic tandem acrylonitrile crossmetathesis/hydrogenation reactions of unsaturated seed oil derivatives to yield α, ω -linear aminoesters and α, ω -linear aminoalcohol was successfully performed by using one single alkene metathesis ruthenium catalyst precursor. The ruthenium residue, arising from the ruthenium cross-metathesis catalyst, with addition of base, allows the very selective catalytic hydrogenation of the nitrile functionality into primary amino methylene group under mild conditions (20 bar of H₂, 80 °C) without addition of ammonium salts. Both long-chain renewable unsaturated nitrile 5, and ester 1 are equally producing good yields of the same C₁₂ aminoester via tandem cross-metathesis/hydrogenation. We have thus shown the transformations of renewable derivatives into industrially applicable polyamide monomers.

Experimental Section

Experimental details are provided in the Supporting Information.

Acknowledgements

The authors are grateful to Arkema and ANRT for a CIFRE Ph.D. grant to X.M., to CNRS, French Ministry MESR, the European Network IDECAT and to the Institut Universitaire de France (PHD) for support, and to Umicore Company for fruitful discussions.

Keywords: fatty esters • hydrogenation • metathesis renewable resources · ruthenium

- [1] a) J.-L. Wasilke, S. J. Obrey, R. T. Baker, G. C. Bazan, Chem. Rev. 2005, 105, 1001; b) S. D. Drouin, F. Zamanian, D. E. Fogg, Organometallics 2001, 20, 5495; c) D. E. Fogg, E. N. dos Santos, Coord. Chem. Rev. 2004, 248, 2365.
- [2] K. Marchildon, Macromol. React. Eng. 2011, 5, 22.
- [3] Nylons are typically obtained from petrochemical products; diacids, diamines, and caprolactone derivatives. Until now, Arkema supplied the only 100% biobased polyamide named Rilsan 11. Recently, several groups (Rhodia, DuPont, DSM, BASF) have announced the production of partially biosourced polyamides.
- [4] a) A. Corma, S. Iborra, A. Velty, Chem. Rev. 2007, 107, 2411; b) C. H. Christensen, J. Raas-Hansen, C. C. Marsden, E. Taarning, K. Egeblad, ChemSusChem 2008, 1, 283; c) P. Gallezot, ChemSusChem 2008, 1, 734; d) U. Biermann, U. Bornscheuer, M. A. R. Meier, J. O. Metzger, H. J. Schäfer, Angew. Chem. 2011, 123, 3938; Angew. Chem. Int. Ed. 2011, 50, 3854.
- [5] Functional olefins are obtained from fossil sources, however, recent examples show that they can also be obtained from renewable materials: For acrylonitrile, see: a) J. Le Nôtre, E. L. Scott, M. C. R. Franssen, J. P. M. Sander, Green Chem. 2011, 13, 807; b) V. Calvino-Casilda, M. O. Guerrero-Pérez, M. A. Bãnares, Green Chem. 2009, 11, 939; c) J.-L. Dubois, US 2010/0048850A1, 2010; For acrolein, see: d) B. Katryniok, S. Paul, V. Bellière-Baca, P. Rey, F. Dumeignil, Green Chem. 2010, 12, 2079; e) J.-L. Dubois, C. Duquenne, W. Holderich, US 7,396,962,B1, 2008; f) J.-L. Dubois, C. Duquenne, W. Holderich, J. Kervennal, US 7,655,818,B2, 2010; For acrylic derivatives, see: g) J.-L. Dubois, C. Duquenne, W. Holderich, US 7,910,771,B2, 2011; h) A. Witsuthammakul, T. Sooknoi, Appl. Catal. A 2012, 413, 109.
- [6] a) R. Malacea, C. Fischmeister, C. Bruneau, J.-L. Dubois, J.-L. Couturier, P. H. Dixneuf, Green Chem. 2009, 11, 152; b) X. Miao, A. Blokhin, A. Pasynskii, S. Nefedov, S. N. Osipov, T. Roisnel, C. Bruneau, P. H. Dixneuf, Organometallics 2010, 29, 5257; c) X. Miao, C. Fischmeister, R. Malacea, C. Bruneau, P. H. Dixneuf, Green Chem. 2011, 13, 2911; see a Review on acrylonitrile cross-metathesis: d) X. Miao, P. H. Dixneuf, C. Fischmeister, C. Bruneau, Green Chem. 2011, 13, 2258.
- [7] a) C. De Bellefon, P. Fouilloux, Catal. Rev. Sci. Eng. 1994, 36, 459; b) F. Mares, J. E. Galle, S. E. Diamond, F. J. Regina, J. Catal. 1988, 112, 145; c) M. Freifelder, Practical Catalytic Hydrogenation: Techniques and Applications, Wiley, New York, 1971, 238; d) T. L. Shih, J. Ruiz-Sanchez, H. Mrozik, Tetrahedron Lett. 1987, 28, 6015; e) F. E. Gould, G. S. Johnson, A. F. Ferris, J. Org. Chem. 1960, 25, 1658; f) B. Staskun, T. V. Es, J. Chem. Soc. C 1966, 531; g) D. J. Ostgard, R. Olindo, M. Berweiler, S. Röder, T. Tacke, Catal. Today 2007, 121, 106; In supercritical CO₂ with Pd/MCM-41: h) M. Chatterjee, H. Kawanami, M. Sato, T. Ishizaka, T. Yokoyama, T. Suzuki, Green Chem. 2010, 12, 87.
- [8] a) S. Nishimura, Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis, Wiley, New York, 2001, Chap. 7, pp. 254-285; b) H. U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner, M. Studer, Adv. Synth. Catal. 2003, 345, 103; c) P. Kukula, M. Studer, H. U. Blaser, Adv. Synth. Catal. 2004, 346, 1487; d) L. Hegedüs, T. Máthé, Appl. Catal. A 2005, 296, 209.
- [9] a) R. A. Grey, G. P. Pez, A. Wallo, J. Am. Chem. Soc. 1981, 103, 7536; b) D. K. Mukherjee, B. K. Palit, C. R. Saha, J. Mol. Catal. 1994, 88, 57; c) K.

Rajesh, B. Dudle, O. Blacque, H. Berke, *Adv. Synth. Catal.* **2011**, *353*, 1479; d) S. Gomez, J. A. Peters, T. Maschmeyer, *Adv. Synth. Catal.* **2002**, *344*, 1037.

- [10] a) X. Xie, C. L. Liotta, C. A. Eckert, *Ind. Eng. Chem. Res.* 2004, *43*, 7907;
 b) S. Takemoto, H. Kawamura, Y. Yamada, T. Okada, A. Ono, E. Yoshikawa,
 Y. Mizobe, M. Hidai, *Organometallics* 2002, *21*, 3897; c) C. Gunanathan,
 M. Hölscher, W. Leitner, *Eur. J. Inorg. Chem.* 2011, 3381.
- [11] a) T. Li, I. Bergner, F. N. Haque, M. Z.-D. Iuliis, D. Song, R. H. Morris, *Organometallics* **2007**, *26*, 5940; b) R. Reguillo, M. Grellier, N. Vautravers, L. Vendier, S. Sabo-Etienne, *J. Am. Chem. Soc.* **2010**, *132*, 7854.
- [12] a) S. Enthaler, K. Junge, D. Addis, G. Erre, M. Beller, *ChemSusChem* 2008, 1, 1006; b) S. Enthaler, D. Addis, K. Junge, G. Erre, M. Beller, *Chem. Eur. J.* 2008, 14, 9491; c) D. Addis, S. Enthaler, K. Junge, B. Wendt, M. Beller, *Tetrahedron Lett.* 2009, 50, 3654; d) S. Das, S. Zhou, D. Addis, S. Enthaler, K. Junge, M. Beller, *Top. Catal.* 2010, 53, 979.
- This work has led to related patent: J.-L. Couturier, J.-L. Dubois, X. Miao,
 C. Fischmeister, C. Bruneau, P. H. Dixneuf, Brevet: FR 2959742A1 20111111; PCT Int. Appl., WO 2011138051A1 20111110, 2011.
- [14] a) H. Baumann, M. Bühler, H. Bochem, F. Hirsinger, H. Zoebelein, J. Falbe, *Angew. Chem.* 1988, 100, 41; *Angew. Chem. Int. Ed. Engl.* 1988, 27, 41; b) H. Guobin, L. Zuyu, Y. Suling, Y. Rufeng, *J. Am. Oil Chem. Soc.* 1996, 73, 1109.
- [15] J.-L. Dubois, J.-P. Gillet, WO2008145941A9, 2008.
- [16] D. Fabritius, H.-J. Schäfer, A. Steinbüchel, Appl. Microbiol. Biotechnol. 1998, 50, 573.
- [17] M. B. Dinger, J. C. Mol, Adv. Synth. Catal. 2002, 344, 671.

Received: February 2, 2012 Revised: April 10, 2012 Published online on

COMMUNICATIONS

X. Miao, C. Fischmeister, C. Bruneau,* P. H. Dixneuf,* J.-L. Dubois, J.-L. Couturier

Tandem Catalytic Acrylonitrile Cross-Metathesis and Hydrogenation of Nitriles with Ruthenium Catalysts: Direct Access to Linear α,ω-Aminoesters from Renewables



Fraternité, Solidarité & complémentarité en Catalyse: Tandem alkene crossmetathesis of acrylonitrile with longchain alkene and hydrogenation catalysis is performed by using a single ruthenium-alkylidene catalyst precursor. The protocol allows the catalytic transformation of unsaturated fatty acids, derivatives of plant oils, into α, ω -aminoesters. A key step involves the reduction of nitrile-ester intermediates into aminoesters, the precursors of polyamides, with alkene metathesis catalyst residue under mild conditions.