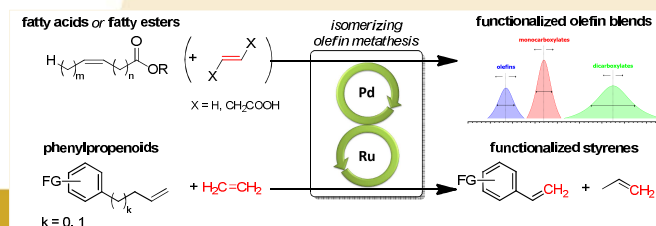


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**Abstract:** A new palladium / ruthenium catalyzed isomerizing olefin metathesis facilitates the efficient synthesis of industrially useful multi-component blends, consisting of functionalized olefins with tunable chain length distributions.<sup>[1]</sup> In the presence of a bimetallic isomerization / metathesis catalyst system, technical quality fatty acids are employed in isomerizing self-metathesis, ethenolysis, or cross-metathesis processes. The resulting product distributions can be tuned, leading to different compositions with quantitative conversions. This way, olefin blends of tailored medium chain lengths become available from renewable resources rather than from crude oil, yielding valuable mono- and dicarboxylates as side products. Phenylpropenoids - naturally occurring terminal olefins can be converted into functionalized styrenes via isomerizing ethenolysis with ethylene being the only side product.

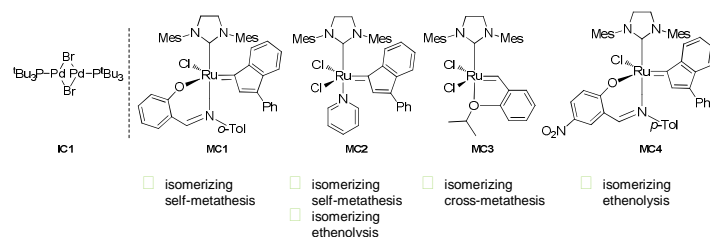


## Method Development: Cooperative Catalysis

The envisioned conversion of uniform fatty acids into tunable functionalized olefin cuts was realized by an isomerizing olefin metathesis. We developed this transformation by screening isomerization catalysts and metathesis catalysts for an efficient combination to establish a balanced tandem reaction.<sup>[1]</sup>

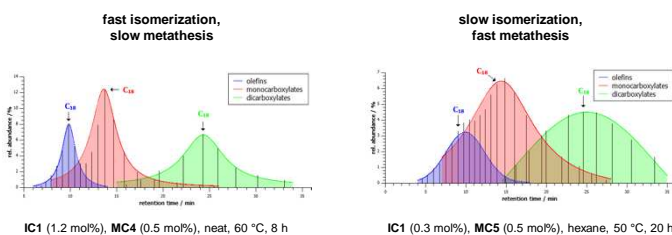


During our studies we identified an isomerization catalyst that is active under conditions of olefin metathesis. Known isomerization catalysts, such as Rh(I) / biphospho<sup>[2]</sup> or Pd(0) / DTBPMB,<sup>[3]</sup> led to low conversions when combined with common ruthenium metathesis catalysts (see below), but did not furnish the desired product distributions. The decisive breakthrough was achieved when combining these Ru catalyst with a dimeric palladium complex [Pd(μ-Br)(<sup>t</sup>Bu<sub>3</sub>P)]<sub>2</sub> **IC1**, facilitating several isomerizing metathesis reactions at loadings below 1 mol%.



## Isomerizing Self-Metathesis of Fatty Acids

Our palladium-based isomerization catalyst gives full conversions of technical grade fatty acids into olefins, unsaturated mono- and dicarboxylates. It is well-compatible with several metathesis catalysts and exhibits an excellent activity at low loadings, mild temperatures, and without activation by e.g. hydrides. The chain length distribution of the resulting product blends (e.g. width and relative concentrations) can be influenced by the choice of catalysts and reaction conditions (shown below for oleic acid, conversions >95%):

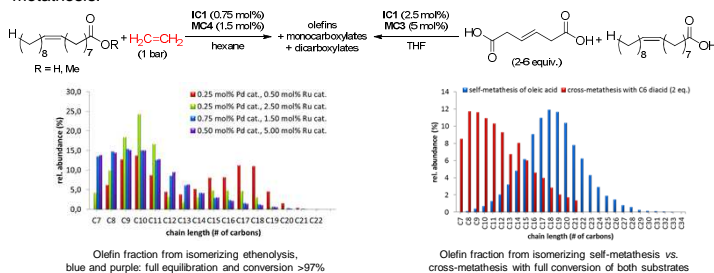


## Literature and further reading (see also www.chemie.uni-kl.de/goossen)

- [1] a) D. M. Ohlmann, N. Tschauer, J.-P. Stockis, K. Gooßen, M. Dierker, L. J. Gooßen, *J. Am. Chem. Soc.* **2012**, *134*, 13716.. b) D. M. Ohlmann, L. J. Gooßen, M. Dierker, *patent application*, **2011**.  
 [2] a) K. Schmitt, F. Gude, Patent US 3723350, **1973**. b) E. J. Vandenberg, Patent US 3058963, **1962**. c) H. P. Rath, H. Mach, M. Röper, J. Stephan, J. Karl, R. Blackborow, Patent WO 016290A2, **2002**. d) K. Maenz, D. Stadermann, *Angew. Makromol. Chem.* **1996**, *242*, 183.  
 [3] a) A. Behr, D. Obst, A. Westfechtel, *Eur. J. Lipid Sci. Technol.* **2005**, *107*, 213. b) D. M. Ohlmann, L. J. Gooßen, M. Dierker, *Chem. Eur. J.* **2011**, *17*, 9508. c) C. Jiménez-Rodríguez, G. R. Eastham, D. J. Cole-Hamilton, *Chem. Commun.* **2004**, 1720. d) D. Quinzler, S. Mecking, *Angew. Chem.* **2010**, *122*, 4402; *Angew. Chem. Int. Ed.* **2010**, *49*, 4306.

## Isomerizing Ethenolysis and Isomerizing Cross-Metathesis

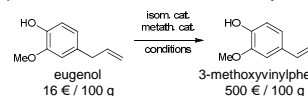
Building on the catalytic isomerization equilibrium, we showed that the chain length distribution can be shifted towards shorter chains by adding a second olefin with a lower number of carbon. The unprecedented isomerizing ethenolysis or cross-metathesis reactions of oleic acid with ethylene or 3-hexenedioic acid yielded full conversions to olefin blends with clearly shorter medium chain lengths compared to the isomerizing self-metathesis.



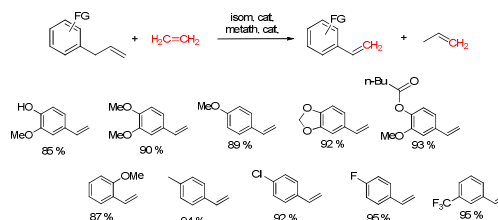
These new methods extend the chemists' toolbox for the efficient utilization of oleochemicals as source of functionalized olefin blends with the help of bimetallic catalysis.

## Isomerizing Ethenolysis of Terminal Olefins

Starting from terminal olefins the isomerizing ethenolysis can be used for shortening olefin chains via stepwise cooperative isomerization and ethenolysis.



This method gives a direct access to valuable functionalized styrenes in very good yield and excellent selectivities under autoclave or microwave conditions proceeding from low-price natural products, with propylene being the only side-product.



This transition metal catalyzed isomerizing ethenolysis is an atom-economical and environmental friendly method for the synthesis of functionalized styrenes.

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