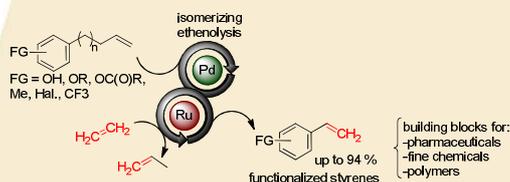


Sabrina Baader,<sup>a</sup> Dominik M. Ohlmann<sup>a</sup> and Lukas J. Gooßen<sup>\*a</sup>

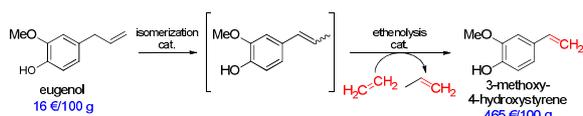
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The combination of  $[\text{Pd}(\mu\text{-Br})(\text{t}\text{-Bu}_3\text{P})_2]_2$  with a Hoveyda-Grubbs II catalyst has been found to efficiently promote the cross-metathesis between substituted alkenes and ethylene, while continuously migrating the double bond along the alkenyl chain. When allylarenes such as the natural products eugenol, safrol or estragol were treated with this catalyst under ethylene pressure, they were cleanly converted into the corresponding styrenes along with propylene gas. This process is of particular value in the context of renewable chemical synthesis, i.e. for incorporating naturally occurring allylarenes, some of which are available on ton scale, into the chemical value chain.

## Importance of Functionalized Styrenes

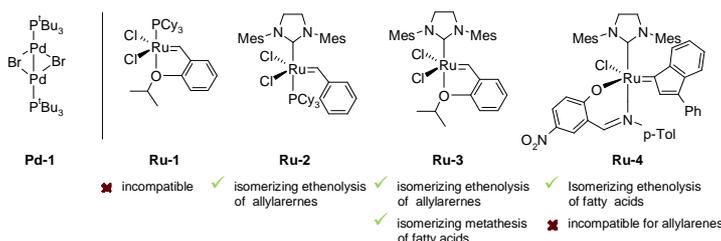
Functionalized styrenes are valuable building blocks for the synthesis of pharmaceutically active compounds, fine chemicals and polymers.<sup>[1]</sup> Several allylarenes are available from natural sources, e.g., eugenol, safrol, estragol or methyleugenol. A possible way to tap into this substrate class as a resource for the synthesis of valuable, functionalized styrenes would be to first migrate the double bond into conjugation with the arene, and then to perform a cross-metathesis with ethylene:



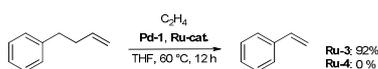
This conversion of the natural product eugenol is a good example of the potential economic impact of this transformation, as the corresponding vinylarene is of substantially higher commercial value than the eugenol starting material.<sup>[2]</sup>

## Method Development: Cooperative Catalysis

In this process, the terminal olefins are continuously converted into a mixture of double-bond isomers. Ethenolysis of this mixture results in a stepwise shortening of the side chain until the desired styrenes are obtained along with volatile, short chain olefins. The recent discovery that the dimeric palladium(II) complex  $[\text{Pd}(\mu\text{-Br})(\text{t}\text{-Bu}_3\text{P})_2]_2$  (**Pd-1**) is a uniquely active isomerization catalyst, which retains its activity in the presence of state-of-the-art olefin metathesis catalysts, finally set the stage for the development of efficient one-pot isomerizing olefin metatheses.<sup>[3]</sup>



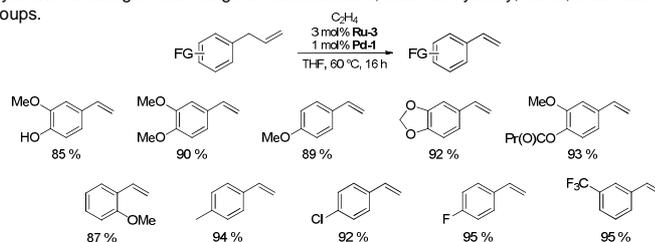
Under the reaction conditions used for the isomerizing ethenolysis of fatty acids (toluene, 60 °C, 10 bar of ethylene, 3 mol% **Ru-4**, 0.75 mol% **Pd-1**) most catalysts gave low conversions. With second generation catalyst **Ru-2** and **Ru-3** full conversion towards the desired product could be arrived without the formation of any unwanted side products.<sup>[4]</sup>



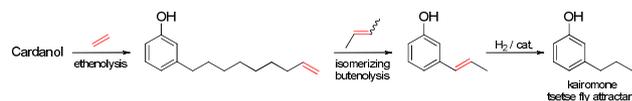
In order to probe the viability of this concept, 4-phenyl-1-butene was treated with an excess of ethylene in the presence of the Pd/Ru catalyst to give the desired styrene in 92% yield.

## Scope of the Isomerizing Ethenolysis and Further Applications

The scope of the new transformation was further investigated starting from various allylarenes bearing a wide range of functionalities, such as hydroxy, ether, ester and halo groups.

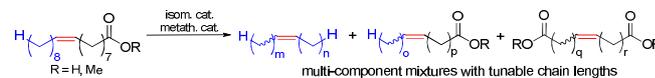


Cardanol is a phenol with a long olefin side chain obtained from anacardic acid, the main component of cashew nutshell liquid (CNSL), a byproduct of cashew nut processing. An interesting application of cardanol would be the formation of a kairomon compound, which could be achieved either via isomerizing ethenolysis or butenolysis.

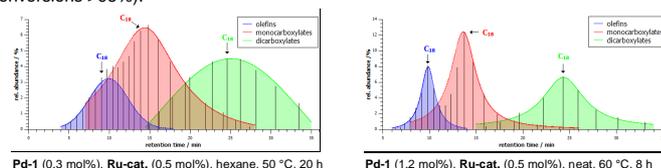


## Isomerizing Metathesis of Fatty Acids

Our new palladium-based isomerization catalyst effects 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%):



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 carbon number such as ethylene.

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

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