Dual-Catalytic Decarbonylation of Fatty Acid Methyl Esters to Form Olefins

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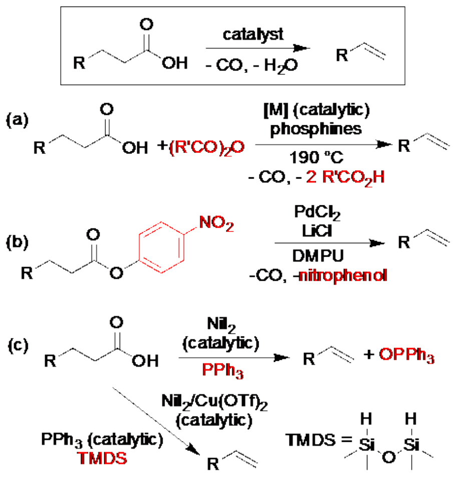
The homogeneous dehydrative decarbonylation of fatty acid methyl esters (FAMEs) to form olefins is reported. In order to facilitate cleavage of the unactivated acyl C–O bond of the alkyl ester, a one pot dual-catalytic directing group strategy was developed through optimization of the individual transesterification and decarbonylation reaction steps.

An important chemical feedstock derived from fossil fuels, olefins also are being targeted for synthesis from sustainable biomass.[1–3] An attractive route is the catalytic dehydrative decarbonylation of bio-derived carboxylic acids (Scheme 1).[4–16] Homogeneous variants of the process typically require prefunctionalization of the carboxylic acid to activate it for the decarbonylation, presumably by facilitating the initial oxidative addition of the catalyst at the acyl C–O bond. A common example uses a stoichiometric amount of a sacrificial anhydride to yield an intermediate mixed anhydride, now susceptible to oxidative addition (Scheme 1a).[5–9,11–15] We recently reported an alternative route whereby *p*-nitrophenol esters of carboxylic acids are converted to *α*-olefins with a palladium catalyst (Scheme 1b), but this process requires the synthesis of the *p*-nitrophenol esters prior to the desired transformation.[17,18] Additive-free conversion of fatty acids to a mixture of olefins has been effected using Ni catalysts, although a terminal reductant (PPh_3 or 1,1,3,3-tetramethyldisiloxane (TMDS)) is required (Scheme 1c).[16] In efforts aimed at developing new, efficient, and potentially industrially relevant variants, we considered fatty acid methyl esters (FAMEs) as potential substrates.

FAMEs are primary constituents of biodiesel and are currently produced via transesterification of vegetable oils or natural triglycerides with methanol.[19] Several deoxygenation routes for FAMEs and triglycerides have been reported using heterogeneous catalysts at high operating temperatures.[20–22] However, most of these strategies suffer from poor reaction control and product selectivity, yielding mixtures of saturated and unsaturated hydrocarbons. A key challenge for the development of homogeneous versions is the stability of the saturated alkyl ester, which renders it recalcitrant toward activation under relatively mild conditions.[23–25] Nevertheless, routes for homogeneous decarbonylation of alkyl esters have been reported using Ru-, Rh- or Ni-based catalysts to form new C–C, C–H or C–Sn bonds.[26–30] Yet, these catalytic systems have not been extended to catalytic decarbonylation of FAMEs to produce olefins.

Scheme 1. Catalytic decarbonylation of carboxylic acids and esters.



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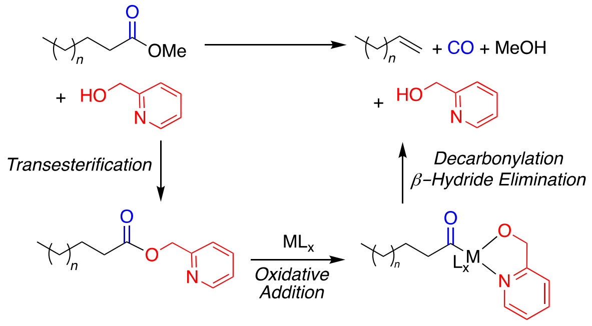
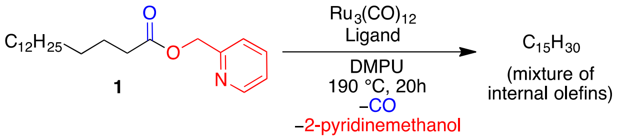
Scheme 2. Proposed dual-catalytic route to decarbonylation of FAMEs.



Herein, we report the application of a dual-catalytic method for the conversion of FAMEs to olefins (Scheme 2), using methyl palmitate as a representative of the broader class. This strategy relies on an initial catalytic transesterification that converts FAMEs to alkyl esters that contain an appended directing group. This directing group would then bind to a second metal-containing catalyst, bringing it in close proximity to the acyl C–O bond and facilitating oxidative addition. Directing group strategies have been used for various catalytic applications,[31–38] including recent reports on the decarbonylation of ketones or alkyl esters.[26–28,39] We report initial development of the dual-catalytic system using high-throughput experimentation (HTE) and larger scale batch experiments, resulting in the successful application to the synthesis of olefins from FAMEs.

As a proof of concept, we initially examined the decarbonylation of a fatty acid ester containing a directing group by evaluating a number of catalysts and ligands through HTE. A palmitic ester containing a pyridine-2-methylene unit (**1**) was targeted, as this directing group was used to enhance both cleavage of the acyl C–O bond and decarbonylation (although these studies did not include FAMEs as substrates and did not report formation of olefins).[26,36] We found that $Ru_3(CO)_{12}$[26,40] was the most active catalyst among a number of others screened (see ESI for details), providing up to 72% conversion of **1** to a mixture of olefins (Table 1, entry 3) with PCy_3 as the optimized ligand. It is worth noting that the reverse reaction has been reported with Ru- and Rh-based catalysts.[32,37,38] Monodentate ligands with a 1:1 ratio of Ru metal centers to ligand were more efficient than bidentate or multidentate ligands (entries 2–4 vs. entries 5–6). In a demonstration of the critical role of the directing group, a variant of **1** with a phenyl ring instead of the pyridyl group was unreactive (only trace amounts of olefin products observed).

Table 1. Decarbonylation of fatty acid esters containing a directing group.[a]



entry	Ligand	Conv. to Olefins (%)[b]
1	none	48
2	PPh_3	65
3	PCy_3	72
4	SIMes[c]	46
5	DPEPhos	21
6	DPPE	<1

[a]Conditions: **1** (0.31 mmol, 1 equiv), $Ru_3(CO)_{12}$ (15 mol % Ru), and ligand (15 mol %) were heated in DMPU (0.5 mL) at 190 °C for 20 h. [b]Conversion of **1** was determined by ^1H NMR spectroscopy. [c]SIMes generated in situ by the deprotonation of 1,3-dimesitylimidazolium chloride with 15 mol % KO^{t}Bu.

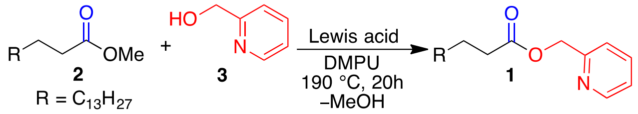
With the identification of conditions for the decarbonylation of **1**, we next examined conditions for the transesterification of methyl palmitate (**2**) with 2-pyridinemethanol (**3**) (Table 2). Interestingly, reactions without a Lewis acid showed reasonably high conversion to **1** of 34% (entry 1). Using HTE methods, several Lewis acids were identified as promising transesterification catalysts (see ESI for more details). Three Lewis acids were scaled up and were all found to increase the conversion of **2** to **1** (entries 2–4).

A time study of the transesterification reaction with $ZnCl_2$ and **2** revealed that 20 h is not needed to reach high conversion. Instead, 39% conversion is obtained after 6 h (see ESI). Additionally, the reaction of **1** with 1 equiv. MeOH in the presence of catalytic $ZnCl_2$ lead to 53% conversion to methyl palmitate **2**. This indicated a possible equilibrium between **2** and **1**. We hypothesized that this reaction could be shifted to the formation of **1** by the removal of MeOH from the reaction. To test this hypothesis, molecular sieves were added to the reaction. Gratifyingly, the addition of molecular sieves improved the average conversion to 50% (entry 5), although results were less consistent between individual runs.

These three equivalent Lewis acid catalysts were then tested for compatibility with the decarbonylation catalysts discussed previously (Table 3). The presence of ZnO or $LaCl_3$ seemed to inhibit decarbonylation of **1**, lowering the conversion to olefins (entries 2–3) relative to the reaction without added Lewis acid (entry 1). On the other hand, $ZnCl_2$ enhanced the decarbonylation conversion, giving a high conversion of 92% (entry 4). We speculate that this enhancement may be due to activation of the C=O bond of the ester by $ZnCl_2$, as previously seen in the literature with an aluminum Lewis acid.[41]

The optimized decarbonylation and transesterification conditions were then applied to the dual-catalytic decarbonylation of FAMEs (Table 4). This dual-catalytic

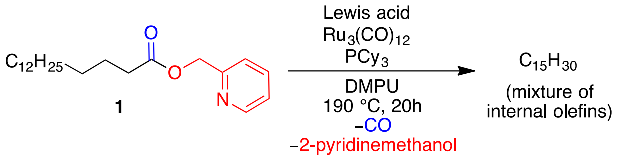
Table 2. Transesterification of methyl palmitate.[a]



entry	Lewis acid	Conv. to **1** (%)[b]
1	none	34
2	$ZnCl_2$	40
3	ZnO	37
4	$LaCl_3$	39
5[c]	$ZnCl_2$	50[d]

[a]Conditions unless specified otherwise: **2** (0.31 mmol, 1 equiv), Lewis acid (25 mol %), and **3** (100 mol %) in DMPU (0.5 mL) were heated at 190 °C for 20 h. [b]Conversion of **2** was determined by ^1H NMR spectroscopy. [c]Three molecular sieves were added (4Å). [d]Reactions with molecular sieves were often inconsistent, with the average presented (see ESI for more information).

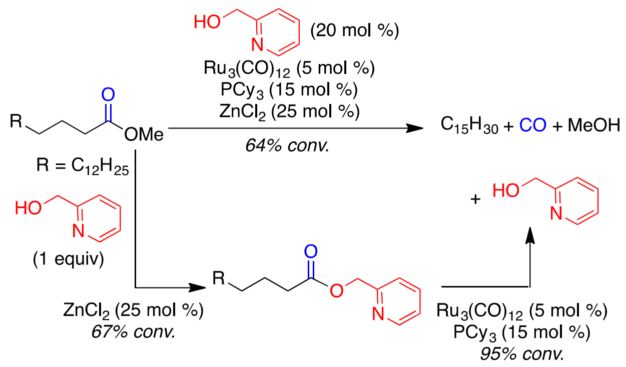
Table 3. Decarbonylation of fatty acid esters containing a directing group in the presence of Lewis acids.[a]



entry	Lewis acid	Conv. to Olefins (%)[b]
1	none	72
2	ZnO	62
3	$LaCl_3$	56
4	$ZnCl_2$	92

[a]Conditions: **1** (0.31 mmol, 1 equiv), Lewis acid (25 mol %), $Ru_3(CO)_{12}$ (15 mol % Ru), and PCy_3 (15 mol %), in DMPU (0.5 mL) were heated at 190 °C for 20 h. [b]Conversion of **1** was determined by ^1H NMR spectroscopy.

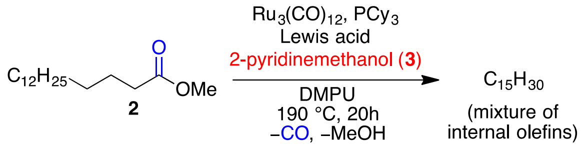
Scheme 3. Optimized conditions for transesterification, decarbonylation, and dual-catalysis, using a sealed 35 mL pressure vessel.



approach was successful in the decarbonylation of methyl palmitate **2**, giving ~38% conversion to a mixture of olefins using catalytic quantities of 2-pyridinemethanol **3** (20 mol %), Lewis acid (25 mol % $ZnCl_2$ or $LaCl_3$), $Ru_3(CO)_{12}$ (15 mol % Ru), and PCy_3 (15 mol %) (Table 3, entries 1–2). Under these conditions, unreacted transesterification product (**1**) was not observed. While the use of ZnO provided comparable conversion to $ZnCl_2$ for the transesterification reaction, it did not match the performance in dual catalysis (entry 3). Unlike the transesterification reaction, a Lewis acid was necessary for the dual-catalytic reaction (entry 4). Similar to the transesterification reactions, addition of molecular sieves increased conversion of **2** to olefins to 47%, presumably due to the removal of MeOH from the reaction solution (entry 5). Further attempts to remove additional MeOH were not found to increase the conversion to olefins (see ESI). The extension of these dual-catalysis conditions for the decarbonylation of palmitic acid was not successful (Table S19).

Further attempts to improve the reaction were explored. Increasing $Ru_3(CO)_{12}/PCy_3$ provided marginal improvement in conversion (entry 6). The addition of catalytic reagents after shorter reaction times similarly provided only slight increases in conversion (see ESI).

Table 4. Dual-catalytic decarbonylation of FAMEs.[a]



entry	Lewis acid	reaction vessel	Conv. to Olefins (%)[b]
1	$ZnCl_2$	8 mL vial	38
2	$LaCl_3$	8 mL vial	39
3	ZnO	8 mL vial	8
4	none	8 mL vial	<1
5[c]	$ZnCl_2$	8 mL vial	47[e]
6[c,d]	$ZnCl_2$	8 mL vial	52[e]
7	$ZnCl_2$	25 mL round bottom	47
8	$ZnCl_2$	35 mL pressure vessel	64

[a]Conditions unless specified otherwise: **2** (0.31 mmol, 1 equiv), Lewis acid (25 mol %), $Ru_3(CO)_{12}$ (15 mol % Ru), PCy_3 (15 mol %), and **3** (20 mol %) in DMPU (0.5 mL) were heated at 190 °C for 20 h. [b]Conversion of **2** was determined by ^1H NMR spectroscopy. [c]Three molecular sieves were added to the reaction vessel (4Å). [d]30 mol % $Ru_3(CO)_{12}/PCy_3$. [e]Reactions with molecular sieves were often inconsistent, with the average presented (see ESI for more information).

Exploration of different reaction vessels led to the discovery of our best conditions. The use of a round bottom flask, with a reflux condenser under a positive N_2 pressure, did not result in a significant increase in the conversion (47%) to olefins (entry 7). However, the use of a sealed 35 mL pressure vessel led to significant improvement in the dual catalytic reaction (entry 8). Examination of all three reactions studied above provided higher conversion in the sealed 35 mL pressure vessel, when compared to the associated conditions in sealed 8 mL vials (Scheme 3). High conversion from **1** to olefins of 95% was achieved, while greatly improved conversion of 64% was observed for the dual-catalytic decarbonylation of **2** to olefins. Current efforts are aimed at trying to understand why the use of this vessel provides such an improvement.

In conclusion, using a combination of high-throughput experiments and scale-up experiments, the dual-catalytic decarbonylation of fatty acid methyl esters (FAMEs) to olefins was accomplished. A combination of a Lewis acid catalyst ($ZnCl_2$) and directing group alcohol (2-pyridinemethanol, **3**) was found to convert methyl palmitate (**2**) to a new alkyl ester containing a directing group (**1**) in up to 67% conversion. Decarbonylation of **1** to form olefins was accomplished using a combination of $Ru_3(CO)_{12}$ and PCy_3, with conversions reaching 95%. One pot reactions were accomplished in which **2** was converted to olefins in up to 64% conversion in the presence of catalytic $ZnCl_2$, **3**, $Ru_3(CO)_{12}$, and PCy_3. These results are distinguishable from other reported directing group decarbonylation methods with respect to their extension to FAMEs, the use of a dual catalysis strategy, and the generation of olefin products. With the ability to convert FAMEs to olefins via homogeneous catalysis now demonstrated, current efforts are aimed at addressing process limitations (e.g. lack of selectivity for terminal olefins, use of a precious metal, Ru), with the ultimate goal being the development of an efficient and large scale process for transforming bio-derived fatty acids or derivatives to useful olefin feedstocks.

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Conflicts of interest

There are no conflicts to declare.

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