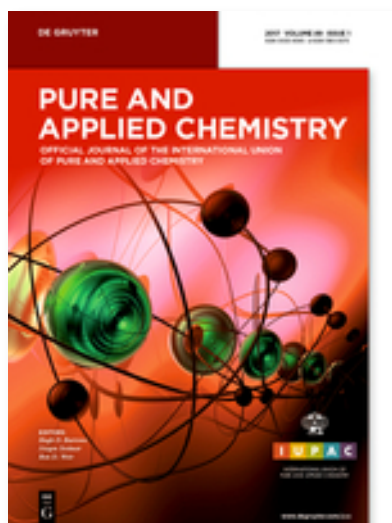


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New catalytic transformations of carboxylic acids

[Lukas J. Gooßen](#) / [Käthe Gooßen](#) / [Nuria Rodríguez](#) / [Mathieu Blanchot](#) /
[Christophe Linder](#) / [Bettina Zimmermann](#)

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A series of metal-catalyzed processes are presented, in which carboxylic acids act as

sources of either carbon nucleophiles or electrophiles, depending on the catalyst employed, the mode of activation, and the reaction conditions. A first reaction mode is the addition of carboxylic acids or amides over C-C multiple bonds, giving rise to enol esters or enamides, respectively. The challenge here is to control both the regio- and stereoselectivity of these reactions by the choice of the catalyst system. Alternatively, carboxylic acids can efficiently be decarboxylated using new Cu catalysts to give aryl-metal intermediates. Under protic conditions, these carbon nucleophiles give the corresponding arenes. If carboxylate salts are employed instead of the free acids, the aryl-metal species resulting from the catalytic decarboxylation can be utilized for the synthesis of biaryls in a novel cross-coupling reaction with aryl halides, thus replacing stoichiometric organometallic reagents. An activation with coupling reagents or simple conversion to esters allows the oxidative addition of carboxylic acids to transition-metal catalysts under formation of acyl-metal species, which can either be reduced to aldehydes, or coupled with nucleophiles. At elevated temperatures, such acyl-metal species decarbonylate, so that carboxylic acids become synthetic equivalents for aryl or alkyl halides, e.g., in Heck reactions.

Keywords: [aryl-metal intermediates](#); [biaryls](#); [carbon nucleophiles](#); [copper catalyst](#); [decarboxylation](#); [enamides](#); [enol esters](#)

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