

CHEMICAL METHODS FOR CARBON DIOXIDE RECYCLING

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INTRODUCTION

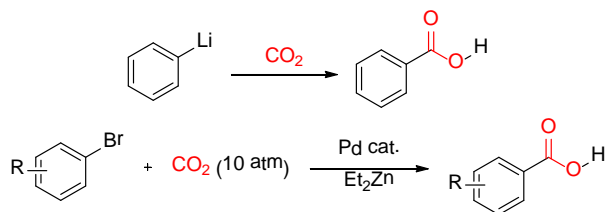
Carbon dioxide is a compound of growing importance to the whole of mankind. The accelerated production and release has been well established, and the current and future impact of this release is the subject of intense study.¹ Anthropogenic CO₂ emissions represent a significant available resource which is being disposed of as waste, rather than utilized as a chemical resource.

Effective utilization requires overcoming the thermodynamic stability inherent to carbon dioxide.² Methods for overcoming this barrier include using high-energy reagents such as organometallic nucleophiles or strained molecules, as well as manipulating unfavorable equilibria. To broaden the scope associated with these methods, an array of approaches must be developed.

SYNTHESIS OF CARBOXYLIC ACIDS AND ESTERS

Carboxylic acids are important compounds across organic chemistry. Traditional approaches to synthesize carboxylic acids include oxidation of pre-functionalized carbon atoms, hydrolysis of nitriles, and addition of highly reactive organolithium or Grignard reagents to carbon dioxide.³

Recent work has enabled the synthesis of these valuable compounds with milder reagents via transition-metal catalysis, allowing for greater functional group compatibility. The Martín group has



Scheme 1. Aryl Halide Carboxylation.

shown that palladium and nickel catalysts can effect the carboxylation of aryl and benzyl halides, respectively (Scheme 1).^{4,5} This method allows for the coupling of arenes bearing sensitive functional groups

such as ketones, esters, and epoxides. The proposed catalytic cycle does not involve the formation of an organozinc species; in fact, upon submission to the reaction conditions, the benzene and toluene were the only observed products.

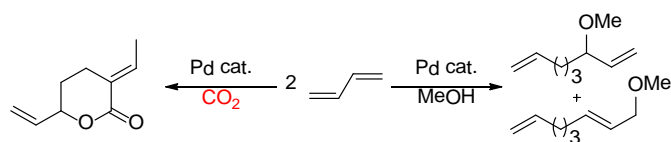
Nolan and Hou have demonstrated the use of Gold and Copper complexes to directly carboxylate C–H bonds of electron-deficient arenes.^{6,7} By using an N-heterocyclic Au(I) hydroxide as the catalyst, a variety of heterocycles and electron-deficient benzene derivatives can be carboxylated, generating the potassium carboxylate and water (Scheme 2). Directly functionalizing a C–H bond avoids the need for pre-installed leaving groups and stoichiometric reducing agent, instead relying on a base to facilitate the activation. A relationship between the pK_a of the C–H bond and the ability of the catalyst to carboxylate

at that position is noted, showing that [(IPr)AuOH] is able to carboxylate a C–H position where the pKa is up to 29.

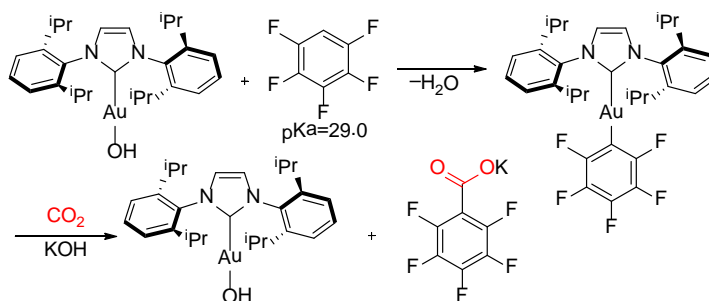
INDUSTRIAL PRODUCTION OF VALUE-ADDED MATERIALS

Telomerization of 1,3-butadiene with CO₂

Palladium-catalyzed telomerization of 1,3-butadiene is a method to generate, atom-economically, functionalized octadienes.⁸ The process involves deprotonation of a protic nucleophile by the π -allyl palladium, followed by nucleophilic attack of the resulting anion on the remaining π -allyl to regenerate the catalyst. This process occurs with carbon dioxide as well, although the major product is a δ -lactone



Scheme 3. Telomerization of 1,3-butadiene.



Scheme 2. C–H Functionalization.

(Scheme 3).⁹ This lactone can be used to produce an array of functionalized chemical feedstock.

Synthesis of Polycarbonates From CO₂

Another approach to overcoming the stability of CO₂ is targeting a product which does not necessitate reduction of CO₂. This is known for urea, formed via an exothermic process from ammonia and CO₂.² Another target of interest would be polycarbonates, which have many applications owing to their desirable physical strength, impact resistance, and biological applications. Current methods for the formation of polycarbonates typically proceed from phosgene and diols, but the copolymerization of CO₂ and epoxides has been demonstrated as early as 1969.¹⁰ Recent advances have allowed for facile preparation of polymers in this way.¹¹

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