

CO₂-Based Reactive Ionic Liquid as Immobilization Agent for Homogeneous Amination Catalysts

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Abstract

The formation of carbon-nitrogen bonds is a challenging task, due to selectivity problems or the utilization of highly reactive substances causing a significant amount of waste. In this regard, highly selective and atom-economic homogeneous catalysis can help to reduce energy costs and waste production. Hydroamination, telomerization, reductive amination, alcohol amination or hydroaminomethylation show great potential for these conversions. However, the separation of the precious transition metal catalysts from the reaction mixture and its potential reuse is of critical importance. By application of a special class of reactive ionic liquids (RIL), the catalyst can be immobilized in the reactive ionic liquid phase, while simultaneously it serves as substrate in the desired amination reactions. These ammonium carbamates consist of a mixture of a primary or secondary amine and carbon dioxide (Figure 1).

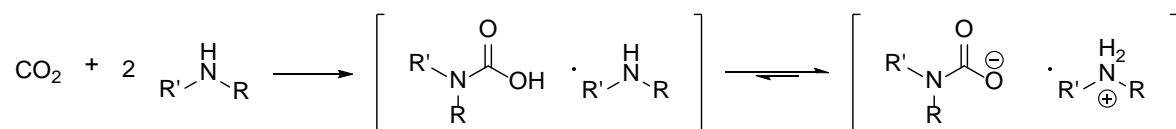


Figure 1: General scheme of the formation and equilibrium of a substituted ammonium carbamate.

One representative of these compounds is dimethylammonium dimethylcarbamate (Dimcarb), which was already investigated for the recycling of a homogeneous palladium catalyst in the hydroamination of β -farnesene and in the telomerization of butadiene.^[1]

Until now there have only been investigations on alkenes and unfunctionalized 1,3-dienes as substrates but there are no insights on the mechanisms and no understanding which species of Dimcarb reacts in the amination reactions. The previous investigations were restricted to palladium catalysts and therefore also restricted in the type of reaction, due to the similarities of hydroamination and telomerization. Nevertheless, based on these preliminary results,^[1] the scope of substrates, catalyst metals, and amination reactions is presented. For the first time, detailed insight on the phase behavior of Dimcarb and the used substrates is given.

[1] T. A. Faßbach, R. Kirchmann, A. Behr, A. J. Vorholt, *Green Chem.* **2017**, *19*, 5243-5249.