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# **Green Chemistry**

# PAPER

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The catalyst in homogeneously catalyzed aminofunctionalizations is often difficult to recycle, making these reactions expensive on an industrial scale. The use of dimethylammonium dimethylcarbamate (*dimcarb*) as a reactive ionic liquid provides an elegant solution to this challenge, as it is substrate and polar phase at the same time. In this work, homogeneously transition-metal catalyzed reactions - specifically hydroamination, telomerization and hydroaminomethylation - are carried out in neat substrates without additional solvents. The ionic character of dimcarb enables the immobilization of the active catalysts in the reactive ionic liquid, using sulfonated ligands. Investigations regarding the hydroamination of 1,3-dienes led to a total turnover number (TTON) of more than 8,700 with  $\beta$ -farnesene in 12 repetitive recycling experiments. The telomerization of 1,3-butadiene was carried out over 30 consecutive runs without any loss of activity, resulting in a TTON of more than 90,000.

## Introduction

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Methylamines are one of the most important building blocks in the chemical industry. Among these, the demand for dimethylamine as building block is the highest on the global market.<sup>1</sup> Its derivatives are used as solvents, agrochemicals and surfactants, such as amine oxides (N-Oxides), betaines or quaternary ammonium compounds (quats).<sup>2</sup> Recent research has demonstrated that building blocks for surfactants can be obtained via the palladium-catalyzed hydroamination of the terpene  $\beta$ -farnesene with dimethylamine.<sup>3</sup> Hydroaminations of 1,3-dienes are typically catalyzed by palladium or nickel complexes with diphosphine ligands.<sup>4–12</sup> The hydroamination of  $\beta$ -farnesene with secondary amines was originally carried out in DMF. As a source for dimethylamine, the respective CO<sub>2</sub>-adduct dimethylammonium dimethylcarbamate (in brief: dimcarb, see Scheme 1) was used. Liquid dimcarb is easy to handle and can be considered an ionic liquid (IL), as ionic form predominates.13,14



Scheme 1 Synthesis and tautomeric forms of dimethylammonium dimethylcarbamate (*dimcarb*).

several advantages. It can be prepared simply by distilling a CO<sub>2</sub>saturated aqueous dimethylamine solution, which makes it significantly cheaper than, for instance, imidazolium salts.<sup>15</sup> Most ILs cannot be purified by distillation.<sup>16</sup> This means they are prone to byproduct contamination, which can accumulate in a continuous process. By contrast, dimcarb can be distilled with ease at moderate temperatures (bp: 68 °C). Using dimcarb as a reactive ionic liquid, i.e. as both the substrate and the solvent, eliminates the need for additional solvents in this homogenously catalyzed reaction. To date, there are several approaches to catalyst recycling in hydroamination reactions, e.g. the use of thermomorphic solvent systems (TMS)7,17, catalyst precipitation<sup>18</sup>, the immobilization on supported ionic liquid phases (SILP)<sup>19</sup> or other heterogeneous supports<sup>20</sup>. If it were possible to overcome the opposing polarities of the ionic dimcarb and the non-polar hydrocarbon farnesene during as well as re-establish them after the reaction, an efficient catalyst recycle would be possible. To realize this concept, three fundamental conditions must be fulfilled:

In contrast to commonly used ionic liquids, dimcarb offers

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- *I.* The substrates must be sufficiently solubilized in the same phase as the catalyst.
- *II.* The reaction can only be catalyzed in the absence of a solvent, if the substrates do not hamper the catalyst both chemically and physically.
- III. After the reaction, products and catalyst must be separated effectively and easily, e.g. by extraction or, ideally, by spontaneous phase separation and decanting.

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E-mail: andreas.vorholt@bci.tu-dortmund.de Electronic Supplementary Information (ESI) available: Characterization of all products and detailed results, including leaching values. See DOI: 10.1039/x0xx00000x

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#### **Results & Discussion**

#### Hydroamination

To address I., one must clarify whether the reaction is to take place in one homogeneous phase or if there is a biphasic reaction mixture. To clarify this, the substrates were weighed in a 300 mL reactor with a sight glass, stirred and heated to 100 °C, which is a typical reaction temperature for hydroaminations. At the beginning both compounds are not miscible and build two clear phases. After heating the mixture to approximately 90 °C, phase behavior changes. Despite a continuously occurring vaporization/condensation of the dimcarb, which makes the solution turbid, the substrate mixture is one homogeneous liquid phase at reaction temperature (Figure 1). This means that the reaction mixture shows phase behavior that is quite similar to thermomorphic solvent systems<sup>21,22</sup> as opposed to liquid/liquid biphasic systems.<sup>23</sup> Another possible explanation for the observed behavior might be the presence of a gasexpanded liquid.<sup>24</sup> In terms of II., the reaction must be carried out in neat substrates. Hydroaminations are typically not carried out in the neat substrates, since high concentrations of amine inhibit the hydroamination catalyst.<sup>3,7,25</sup> Surprisingly, the hydroamination of farnesene with dimcarb not only works well in DMF, but can be carried out easily without additional solvents. Subsequent to optimizations to the reaction parameters, the reaction was even carried out using only 0.1 mol% of palladium, which is an eighth of the original amount of palladium and diphosphine ligand DPPB (=1,4-bis(diphenylphosphino)butane see Figure 2). The reaction leads to N,N-dimethyl farnesylamines at a yield of 89% after 4 hours (Scheme 2). This constitutes an increase in the turnover frequency (calculated as moles of products per mole of palladium/hour) from 29 h<sup>-1</sup> in the reaction carried out in DMF to 223 h<sup>-1</sup> in dimcarb. Research has shown that some transition metal catalyzed reactions show higher reaction rates when carried out in ionic liquids.<sup>26</sup> Thus, it is plausible that these good results are consequences of an interaction of the reactive ionic liquid with the catalyst and/or a transition state in the catalytic cycle. After the reaction takes place and the mixture is cooled to room temperature, a spontaneous phase separation occurs. This phase behavior is very favorable because it enables product/catalyst separation, contributing to III.



 $\label{eq:DPPB: R = H} \begin{array}{l} \textbf{DPPBTS: R = H} \\ \textbf{DPPBTS: R = SO_3Na} \end{array}$  Figure 2 Structure of the applied DPPB and the DPPBTS ligand.

In the present case, the upper layer consists almost exclusively of the desired products and non-converted farnesene, while the excess dimcarb forms the lower phase. The catalyst was recycled successfully by removing the product phase, adding new substrate and restarting the reaction, which showed catalytic activity in three recycling experiments. Unfortunately, from the second run on, the yields drop by one third after each recycle (Figure 3).

ICP-OES measurements indicate that this is the result of severe palladium leaching into the non-polar product phase in nearly the same quantity (detailed results of yields and leaching can be found in the supporting information). In order to effectively immobilize the catalyst complex in dimcarb, which is predominantly available in the ionic form, the tetra-sulfonated analog ligand DPPBTS (=1,4-bis(diphenylphosphino)butanetetra-sulfonate, see Figure 2), was employed. The first recycling run yielded slightly more product than in the initial run, which was likely caused by small amounts of the product remaining in the catalyst phase. After the dimcarb is saturated with products, the isolated yields are maintained. The next eight runs show consistently high catalytic activity, which is backed by very little to no (< 0.1%) leaching of palladium and phosphorous into the product phase (for detailed data of the ICP-OES measurements, see supporting information). After the eighth run, the catalyst phase turned from a light yellow color to dark orange, indicating a decomposition of the catalyst. According to <sup>31</sup>P-NMR the ligand ( $\delta$  = -15.25) was oxidized to the phosphine oxide ( $\delta$  = +32.41), most probably due to oxygen contamination.<sup>27</sup> Another plausible explanation would be the presence of peroxides in one of the substrates.28

Figure 1 Dimcarb and  $\beta$ -farnesene are biphasic at 40 °C (left) and one phase at 100 °C (right) at 10 bar, without stirring.





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Oxidation from P<sup>III</sup> to P<sup>V</sup> results in the decomposition of the active catalyst, most probably due to the loss of the ligand's capability to coordinate to the palladium. This is also indicated by increased palladium leaching into the non-polar phase at a rate of 1% and 2% respectively in recycling runs 9 and 10. The amount of leached palladium cannot explain the extent of the loss in catalytic activity, but it proves the ligand required for catalytic conversion is no longer intact. It should be clearly stated that neither the metal nor the ligand was replenished at any time. However, an average turnover frequency (TOF) of 293 h<sup>-1</sup> (calculated as moles of products per mole of palladium and hour) was achieved in the first eight recycling runs. This significantly outperforms other approaches, such as SILP.<sup>29,30</sup> Overall the total turnover number (TTON) in these recycling experiments was 8,724 (calculated as moles of desired product per mole of employed palladium), which represents a tenfold increase as compared to batch experiments. The promising results achieved using  $\beta$ -farnesene as a renewable substrate for hydroamination led to the next step, in which the concept presented was extended to other substrates with 1,3-diene units (see Scheme 3 for reaction and Table 1 for results).



Scheme 3. General hydroamination reaction of conjugated 1,3-dienes with dimcarb.

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Table 1. The hydroamination of 1,3-dienes with dimcarb according to Scheme de Onlin
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1.2 Diana		Average Yield over four
1,3-Diene	ĸ	recycling experiments / %
isoprene	Me	77
β-myrcene	C <sub>6</sub> H <sub>11</sub>	72
β-farnesene	C11H19	88 <sup>[a]</sup>

Reaction conditions: 0.1 mol% Pd(tfa)2; ligand=1,4-bis(diphenylphosphino)butanetetra-sulfonate. metal/ligand=1/4. ndimcarb=45 mmol. n1.3-diene=15 mmol. T=100 °C. t=3 h, 500 rpm, results given based on substrate and determined by GC-FID using dodecane (isoprene and  $\beta$ -myrcene) and decane ( $\beta$ -farnesene) as internal standard

Recycling conditions: Dimcarb was refilled to 45 mmol (addition of 7.5 mmol). phase separation at room temperature under schlenk technique, addition of 15 mmol 1,3-diene, and restart of the reaction. The isoprene product was extracted with 2 mL cyclohexane.

[a]: Average yield of the first 8 recycling runs, see Figure 3.

As is shown with the 1,3-dienes isoprene and  $\beta$ -myrcene, the catalytic system works well without optimizing the reaction parameters. Recycling was carried out four consecutive times for each substrate after the initial reaction. Again neither the metal nor ligand was replenished and negligible leaching of the palladium and phosphorous into the product phase occurred according to ICP-OES measurements. With 72% ( $\beta$ -myrcene) and 77% (isoprene) respectively, the average yield of hydroamination products over the course of four consecutive recycling experiments (initial run is omitted, for detailed results, see ESI) is high. The results using isoprene demonstrate that the concept of the solvent-free reactions with subsequent recycling works for short chain 1,3-dienes as well. The product of dimethylamine and isoprene is soluble in the catalyst phase, but can easily be separated by extraction with cyclohexane without interfering with the homogeneous catalyst. This shows that the products do not need to be insoluble in the dimcarb phase to be effectively separated from the catalyst and to subsequently recycle the latter.

#### Telomerization

The next step entailed converting short chain olefins, such as 1,3-butadiene, with amines using homogenous transition metal catalysts. Telomerization is a promising reaction in connection with very similar catalysts and substrates. It is a dimerization of 1,3-dienes to 2,7-octadienyls with the addition of an H-acidic nucleophile.<sup>31,32</sup> The most common 1,3-diene used is 1,3-butadiene, along with alcohols<sup>33–36</sup>, amines<sup>37,38</sup> and even carbon dioxide<sup>39,40</sup>. Besides 1,3-butadiene, a common diene is isoprene<sup>41–44</sup>, but 1,3-piperylene<sup>45</sup>, 1,3-hexadiene<sup>46</sup>, and  $\beta$ -myrcene<sup>47,48</sup> are reported as well. Palladium modified with phosphine ligands is typically used as the catalyst, though in recent years the use of N-heterocyclic ligands has been investigated extensively.49-52 Although comprehensive studies have been conducted on the separation of products and catalysts in telomerization, only a few examples exist that demonstrate efficient catalyst recycling.35,53-55 Carrying out the telomerization of 1,3-butadiene with dimcarb means to work with short-chain olefins, which are soluble in dimcarb and relatively polar resulting products (Scheme 4), which are soluble in the catalyst phase as well.

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Scheme 4 Telomerization of 1,3-butadiene with dimcarb to the linear (*n*-) and the branched (*iso*-) products

This provides opposing conditions compared to the case of the hydroamination of  $\beta$ -farnesene with dimcarb, in which only the catalyst was soluble in the polar phase at room temperature. Since triphenylphosphine is active for the telomerization of 1,3-butadiene with amines<sup>56</sup> and the respective sulfonated form TPPTS (= triphenylphosphine-trisulfonate) is widely used, it has already been successfully used in the biphasic selective mono-telomerization of 1,3-butadiene with ammonia<sup>57</sup>, which was chosen as the catalytic system as a result. The recyclability of the active catalyst was tested with this system. Cyclohexane was used as extraction agent to overcome the miscibility of the telomerization products with dimcarb. Stable catalytic activity of the Pd/TPPTS complex was achieved for the telomerization of 1,3-butadiene over the course of 30 runs (Figure 4).



**Figure 4.** Isolated product yields of the palladium catalyzed telomerization of 1,3-butadiene with dimcarb to *N*,*N*-dimethyl octadienylamines.

Reaction conditions: Precursor=Pd(acac)<sub>2</sub>, 0.03 mol% based on 1,3-butadiene, ligand=TPPTS (=triphenylphosphine-trisulfonate), metal/ligand=1/4,  $n_{dimcarb}$ =30 mmol,  $n_{1,3-butadiene}$ =38 mmol, T=80 °C, t =2 h, 500 rpm, results determined by GC-FID using dibutyl ether as internal standard.

*Recycling conditions*: Extraction of the product with cyclohexane (2x2 mL), dimcarb was refilled to 30 mmol (addition of 11 mmol), addition of 38 mmol 1,3-butadiene, restart of the reaction.

Decreases in activity or selectivity were not observed. After the 30<sup>th</sup> run, the recycling experiment was stopped defiberately.<sup>2</sup>An average desired product yield of 90% was obtained. The selectivity in all runs was 99%, resulting in a product-related TTON (converted moles of 1,3-butadiene to the desired products per mole of palladium) of 90,712. The linearity of the resulting products (calculated as the share of *n*-product among the yielded products) was consistent at 92%. Regarding the ICP-OES measurements, little to no palladium or phosphorous was leached into the cyclohexane phase, which again made replenishing the metal and ligand unnecessary. An average TOF (calculated as converted moles of 1,3-butadiene per mole of palladium and hour reaction time) of 1,436 h<sup>-1</sup> was achieved over the course of 31 consecutive reactions, which means this reaction system is industrially viable.<sup>58</sup>

Overall these results demonstrate that the reactive ionic liquids approach, with its excellent total turnover numbers and spacetime-yields that lead to potential valuable products, is suitable for industrial processes using cheap and readily available catalysts and substrates.

#### Hydroaminamethylation

To open further perspectives for the presented approach, hydroaminomethylation (HAM) was investigated, which is completely different from the examples presented so far. HAM a tandem catalyzed reaction, consisting of the is hydroformylation of an olefin followed by a reductive amination of the obtained aldehyde (Scheme 5).59,60 The intention was to expand the presented method to other transition metals (rhodium), substrates (olefins) and gaseous compounds (syngas). In this case, 1-dodecene was used as the olefin and [Rh(cod)Cl]<sub>2</sub>/sulfo-XantPhos as the catalytic system. After some preliminary optimizations (for results, see Supporting Information), particularly with regard to aldol condensation as a side reaction, a yield of 40% of the dimethyl tridecylamine was achieved. This reaction was carried out over the course of five recycling runs after the initial reaction, with an average yield of 32%. Since the products are non-polar, no extracting agent was required. Although a decrease in activity was observed, almost no leaching of the precious catalyst into the product phase (< 0.1%) was detected. Accordingly, reactions that include gaseous components can be conducted using this system and transition metals other than palladium are immobilized effectively in the dimcarb phase as the catalytically active species.



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## Conclusion

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The investigations presented regarding amination reactions in the reactive ionic liquid dimethylammonium dimethylcarbamate (dimcarb) demonstrate two striking advantages for homogenously catalyzed reactions. Firstly, the reactions can be carried out without additional solvents, because dimcarb, as a reactive ionic liquid, acts as both the solvent and the substrate and does not interfere with the catalyst in the examples presented. This is highly favorable and rarely described for homogenously catalyzed amination reactions. The system's highly efficient catalyst recycling using sulfonated ligands is the second advantage. Without the need for auxiliaries, virtually no leaching of the metal or ligand into the product phases occurs and the catalyst is retained as the catalytically active species. This makes this new approach suitable for continuously operated processes. In terms of hydroaminations, this might be carried out using flow conditions, as these have been proven to be an appropriate mode for these reactions.<sup>17</sup> Especially with regard to the telomerization of 1,3-butadiene, continuously high conversions and selectivities were achieved. A deeper understanding of this reaction must be obtained at miniplant scale to investigate long-term phenomena. Furthermore, the telomerization of other 1,3-dienes, such as isoprene and  $\beta$ -myrcene, would result in dimethyl branched C<sub>10</sub>-amines (isoprene) or highly branched  $C_{20}$ -amines ( $\beta$ -myrcene), which might be interesting products as well. The hydroaminomethylation results demonstrate that this strategy is also compatible with carbonylation chemistry in principle, as demonstrated with the hydroaminomethylation. Future investigations will focus on broadening the spectrum of applicable amines. Since most ammonium carbamates are solid at room temperature<sup>61</sup>, conducting phase separation at elevated temperatures must be considered. Furthermore, additional reactions that may benefit from this method, e.g. aminocarbonylations<sup>62,63</sup> or aminations of alcohols<sup>64</sup>, will be investigated.

## **Experimental Section**

Chemicals were purchased from *Acros Organics* (Geel, Belgium), *Sigma-Aldrich* (Steinheim, Germany) and *TCI* (Tokyo, Japan). 1,3-butadiene was obtained from *Messer* (Bad Soden, Germany),  $\beta$ -farnesene was provided by *Clariant* (Frankfurt a.M., Germany). All substrates (except 1,3-butadiene) and the cyclohexane were dried over molecular sieves and degassed by bubbling argon through the liquids prior to use.

The catalytic experiments were carried out in a custom made steel autoclave. The metal precursor and the ligand were weighed directly into the pot. The reactor was flushed with argon and DimCarb and the respective substrates were subsequently added with an argon counter flow. For the telomerization experiments the reactor was closed and 1,3-butadiene was added volumetrically *via* a pressure-resistant tube. To determine the accurate mass of the added 1,3-butadiene, the reactor was weighed before and after adding the 1,3-butadiene. The reactor was subsequently pressurized

with 5 bar argon. The reaction mixture was transferred intonal schlenk flask to recycle the catalyst. The extraction solve at was added and removed from the dimcarb phase after separation as needed. The consumed dimcarb was replenished, the polar phase was transferred back into the reactor and new substrate was added. All products were purified by silica gel column chromatography and calibrated for GC-FID analysis with internal standard. Routine gas chromatographic analyses were performed on an *Agilent 7890B* instrument (Santa Clara, USA) equipped with a flame ionization detector (FID) and a HP-5 capillary column (30 m, diameter 0.32 mm, film thickness 0.25 µm) connected to an auto sampler (*7693*) and an injector (*G4513A*). GC-MS analyses of the products were carried out on an Agilent *5977A MSD* (70 eV).

NMR spectra were recorded on *Bruker DRX* spectrometers. CDCl<sub>3</sub> was used as solvent and standard for chemical shifts, purchased from *Deutero*.

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