A new air-stable zinc complex based on a 1,2-phenylene-diimino-2-cyanoacrylate ligand as an efficient catalyst of the epoxide–CO₂ coupling†

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A novel zinc complex based on a diethyl 1,2-phenylene-diimino-2-cyanoacrylate ligand is a very efficient catalyst in the conversion of epoxides with CO₂ to organic carbonates, in the case of propylene carbonate also under mild reaction conditions. Using cyclohexene oxide leads to the formation of alternating aliphatic polycarbonates in good yields.

Carbon dioxide, undeniably a greenhouse gas and a significant contributor to climate change, is in the focus of an ever increasing number of studies, from an academic- as well as from a more industrial and profit-oriented point of view. In the meantime it is well accepted that CO₂ emissions are directly connected to human activities, the major source being the combustion of fossil fuels. For this reason several initiatives have been undertaken trying to turn back time, with a focus on carbon dioxide storage and its utilisation as a solvent or a chemical C1-building block. One promising reaction using CO₂ is its coupling reaction with epoxides leading to two types of organic carbonates: monomeric cyclic carbonates and aliphatic polycarbonates (Scheme 1). Both carbonate classes are useful products: the former for example used as high-boiling point solvents or electrolytes in lithium ion cells, and the latter as a complement to the more common aromatic polycarbonates or as starting material for further specialty materials (e.g. mid-segment in “environmentally-friendly” polyurethanes).

In the literature numerous catalytic systems, homogeneous as well as heterogeneous, have been reported for the coupling of epoxides with CO₂. To have a chance to compete with known systems, a good catalyst has to be versatile, easy-to-synthesise and easy-to-handle, highly selective and, considering the rising energy costs, it should also be active under mild conditions.

We have already reported the successful use of iron and aluminium complexes in the coupling of CO₂ with epoxides, the catalysts involving a simple N₂O₂-ligand displaying cyano-acrylate and malonate functionalities. Considering the preponderant role of some zinc catalysts in the formation of organic carbonates and especially polycarbonates like e.g. zinc glutarate, zinc β-diminate and the structurally similar zinc 3-amino-2-cyanoimidoacrylates, it was interesting to synthesise related N₂O₂-zinc complexes and to test their catalytic activity in the CO₂-epoxide coupling. Surprisingly there has been no report up to now of such complexes. We report here the first X-ray structure determination of such a zinc-N₂O₂ cyano-acrylate complex and the first successful utilisation of this air-stable complex in the formation of organic carbonates also under mild reaction conditions.

Synthesis

The formation of the zinc catalyst 2 is shown in Scheme 2. Ligand 19 was reacted in THF, under argon, with diethylzinc (as hexane solution) to deliver the zinc complex 2, which is air-stable and easy-to-handle. TGA measurements reveal that 2 is stable up to 300 °C without significant weight loss.

Single crystals suitable for a crystal structure analysis could be isolated from a concentrated DMSO solution, showing that complex 2 displays a tetragonal pyramidal coordination geometry around the metal centre, with one oxygen-bound dimethyl sulfoxide molecule in the axial position and the
N\textsubscript{2}O\textsubscript{2}-ligand occupying the equatorial plane (Fig. 1, more details in ESI\textsuperscript{†}). This structure is the first one involving zinc and a N\textsubscript{2}O\textsubscript{2} ligand with amine and ester functions, while the bulk of the other documented Zn/N\textsubscript{2}O\textsubscript{2} + L structures involve the more common salen/salophen-ligands (with phenol and aldime functionalities).\textsuperscript{9,10}

Catalytic tests

Using catalyst 2 for the conversion of propylene oxide (PO) with CO\textsubscript{2} results in the selective production of the corresponding cyclic carbonate (propylene carbonate, PC; Table 1).

The presence of a cocatalyst is necessary as it is usually the case for almost all of the related catalytic systems.\textsuperscript{11,12} Ionic tetrabutyl ammonium salts are very active in our case. Especially Bu\textsubscript{4}NI is very successful (entries 7, 10–19) probably due to the high nucleophilicity of the anion. Along these lines, DFT studies by Kleij et al. reported higher energy values for transition states involving bromide than for iodide.\textsuperscript{11,13} Plausibly, the conversion rates in the presence of chloride-containing cocatalysts were considerably lower. The neutral 4-(dimethylamino)-pyridine (DMAP) and methylimidazole (MeIm) failed to deliver carbonates probably due to a strong interaction of the cocatalysts with the metallic centre as indicated by Darensbourg et al. (entries 2, 3).\textsuperscript{14,15}

The variation of the reaction conditions (\( T, p, \text{cat}\% \), time) underlined the efficiency of the combination of zinc complex 2/Bu\textsubscript{4}NI. Modifying the catalyst/cocatalyst concentration showed that the catalyst is highly efficient: at a catalyst-to-epoxide ratio as low as 1 to 10.000 (0.01 mol%), a cyclic carbonate yield of 64% could be still reached (entry 11). The temperature screening, using a 0.2 mol% catalyst concentration, showed that the system is highly active, already reaching high yields of PC at 40 °C (93%, entry 14). At 30 °C (room temperature at the time the experiment was performed)

\begin{table}[h]
\centering
\begin{tabular}{cccccccc}
Entry & Cat./Cocat. & \( T \) (°C) & \( P \) (bar) & Cat. conc\textsuperscript{a} (mol%) & \( t \) (h) & Yield\textsuperscript{b} (%) & TON & TOF (h\textsuperscript{-1}) \\
\hline
1 & 2 & 80 & 50 & 0.2 & 20 & 20 & 8\% & 38 \\
2 & 2/DMAP & 80 & 50 & 0.2 & 20 & 8\% & 27 \\
3 & 2/MeIm & 80 & 50 & 0.2 & 20 & 6\% & 16 \\
4 & 2/PPNCl & 80 & 50 & 0.2 & 20 & 3\% & 261 \\
5 & 2/Bu\textsubscript{4}NI & 80 & 50 & 0.2 & 20 & 52\% & 106 \\
6 & 2/Bu\textsubscript{4}NI & 80 & 50 & 0.2 & 20 & 99\% & 493 \\
7 & 2/Bu\textsubscript{4}NI & 80 & 50 & 0.2 & 20 & 99\% & 495 \\
8 & 2/Bu\textsubscript{4}NI & 80 & 50 & 0.1 & 20 & 69\% & 690 \\
9 & 2/Bu\textsubscript{4}NI & 80 & 50 & 0.1 & 20 & 97\% & 966 & 48.3 \\
10 & 2/Bu\textsubscript{4}NI & 80 & 50 & 0.1 & 20 & 64\% & 6357 \\
11 & 2/Bu\textsubscript{4}NI & 80 & 50 & 0.01 & 20 & 99\% & 496 \\
12 & 2/Bu\textsubscript{4}NI & 100 & 50 & 0.2 & 20 & 99\% & 490 \\
13 & 2/Bu\textsubscript{4}NI & 80 & 50 & 0.2 & 20 & 98\% & 490 \\
14 & 2/Bu\textsubscript{4}NI & 80 & 50 & 0.2 & 20 & 93\% & 446 \\
15 & 2/Bu\textsubscript{4}NI & 80 & 50 & 0.2 & 20 & 58\% & 288 \\
16 & 2/Bu\textsubscript{4}NI & 80 & 50 & 0.1 & 10 & 95\% & 954 & 95.4 \\
17 & 2/Bu\textsubscript{4}NI & 80 & 50 & 0.1 & 3 & 84\% & 842 & 280.7 \\
18 & 2/Bu\textsubscript{4}NI & 80 & 50 & 0.1 & 1 & 74\% & 744 & 744.0 \\
19 & 2/Bu\textsubscript{4}NI & 80 & 2 & 0.2 & 20 & 20\%\textsuperscript{c} & 100 \\
20 & 2/Bu\textsubscript{4}NI & 80 & 2 & 0.1 & 20 & 63\% & 604 \\
21 & 2/Bu\textsubscript{4}NI & 80 & 2 & 0.2 & 20 & 88\% & 439 \\
\end{tabular}
\caption{Conversion of propylene oxide with CO\textsubscript{2} to propylene carbonate}
\end{table}

\textsuperscript{a}Catalyst : cocatalyst 1 : 1. \textsuperscript{b}Determined by subtracting the catalyst weight from the obtained product weight after removing epoxide remainders in vacuum and checking the purity with \textsuperscript{1}H NMR. \textsuperscript{c}Also contains polypropylene ether. Yield is estimated by \textsuperscript{1}H NMR in benzene \textsubscript{d}\textsubscript{6} with an internal standard (tetrachloroethane).\textsuperscript{5}
propylene carbonate could be still isolated in a 58% yield (entry 15). Lowering the catalyst concentration (0.1 mol%) lead to a similar conversion/temperature trend (see the ESI†). Working with 0.1 mol% of catalyst and stopping the reaction at half the reaction time (10 h) shows once again how effective the combination of zinc complex 2/Bu4NI actually is (entry 16). Shorter reaction times lead to slightly smaller yields (entries 17, 18). For these particular tests the related TOF values are shown in the table. Especially the TOF after one hour underlines the efficiency of the catalyst. Interestingly, performing the screening test at 80 °C and under only 2 bar CO2 leads to the formation of poly(propylene ether) as a side-product (entry 19). This can be avoided by running the reaction at 40 °C and adjusting the amount of catalyst 2 (0.2 mol%); propylene carbonate could be then isolated with an 88% yield (entries 20 and 21).

Using cyclohexene oxide (CHO) as a substrate results in mixtures of cyclic carbonate (CHC) and aliphatic polycarbonates (PCHC). The results from the screening tests with CHO are compiled in Table 2. The polycarbonates formed using catalyst 2 displayed no polyether regions in the 1H NMR, being displayed no polyether regions in the 1H NMR, being

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat./Cocat.</th>
<th>Estimation by 1H NMR°</th>
<th>Precipitated polymerb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CHC</td>
<td>PCHC</td>
</tr>
<tr>
<td>1</td>
<td>2/Bu4NI</td>
<td>0%</td>
<td>11%</td>
</tr>
<tr>
<td>2</td>
<td>2/Bu4Br</td>
<td>30%</td>
<td>15%</td>
</tr>
<tr>
<td>3</td>
<td>2/Bu4NBr</td>
<td>24%</td>
<td>3%</td>
</tr>
<tr>
<td>4</td>
<td>2/Bu4NCI</td>
<td>0%</td>
<td>33%</td>
</tr>
<tr>
<td>5</td>
<td>2/PPNCl</td>
<td>0.4%</td>
<td>58%</td>
</tr>
<tr>
<td>6c</td>
<td>Al N2O2(cyano-acrylate)/Bu4NBr</td>
<td>1%</td>
<td>99%</td>
</tr>
</tbody>
</table>

Reaction conditions: 80 °C, 50 bar, c(cat cocat) 1.0 mol%, 20 h. ° Products were estimated using 1H NMR in benzene d6. b Precipitation was applied by dissolving the raw products in as much dichloromethane as needed to get them fully dissolved and then adding 130 ml of methanol. c 80 °C, 50 bar, c(cat cocat) 0.2 mol%, 20 h, catalyst was added in a solution of 2 ml dichloromethane.

Table 2 Conversion of cyclohexene oxide with CO2 to cyclohexene carbonate and poly(cyclohexene carbonate) (100% carbonate linkage)

Conclusions

Zinc complex 2 is an easy-to-handle catalyst for the conversion of epoxides with carbon dioxide. In the case of propylene oxide, the cyclic carbonate is formed selectively in high yields even under mild reaction conditions and low catalyst loadings. The utilisation of an ionic cocatalyst is obligatory for the success of the catalytic reaction. The nature of the anion plays a role in the product distribution: the higher the nucleophilicity, the better is the cyclic carbonate yield. The same trend could be observed changing from propylene oxide to cyclohexene oxide. Using Bu4NI and Bu4NBr as cocatalysts gives mixtures with cyclic carbonates as major products. In contrast the utilisation of cocatalysts containing chloride as a harder
Lewis base (PPNCl and Bu₄NCl) leads to the formation of pure alternating polycarbonates.

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Notes and references

9 See ESI.f
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