A new air-stable zinc complex based on a 1,2-phenylene-diimino-2-cyanoacrylate ligand as an efficient catalyst of the epoxide−CO$_2$ 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 CO$_2$ 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 CO$_2$ 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[1] and its utilisation as a solvent or a chemical C1-building block.[2] One promising reaction using CO$_2$ 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
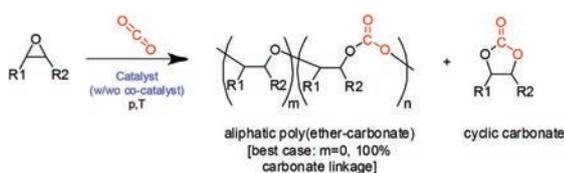
polycarbonates or as starting material for further specialty materials (*e.g.* mid-segment in "environmentally-friendly" polyurethanes).[3]

In the literature numerous catalytic systems, homogeneous as well as heterogeneous, have been reported for the coupling of epoxides with CO$_2$.[4] 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 CO$_2$ with epoxides, the catalysts involving a simple N$_2$O$_2$-ligand displaying cyano-acrylate and malonate functionalities.[5,6] Considering the preponderant role of some zinc catalysts in the formation of organic carbonates and especially polycarbonates like *e.g.* zinc glutarate, zinc β-diiminate and the structurally similar zinc 3-amino-2-cyanoimidoacrylates,[7] it was interesting to synthesise related N$_2$O$_2$–zinc complexes and to test their catalytic activity in the CO$_2$–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–N$_2$O$_2$ cyano-acrylate complex and the first successful utilisation of this air-stable complex in the formation of organic carbonates also under mild reaction conditions.

Scheme 1 Possible products of the reaction of carbon dioxide with epoxides.

Synthesis

The formation of the zinc catalyst **2** is shown in Scheme 2. Ligand **1**[8] 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.[9]

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
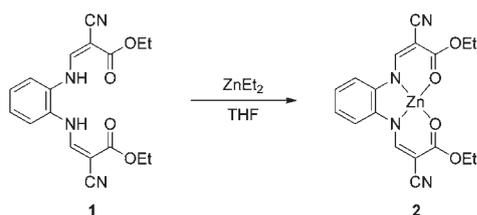
Scheme 2 Synthesis of the zinc complex **2**.
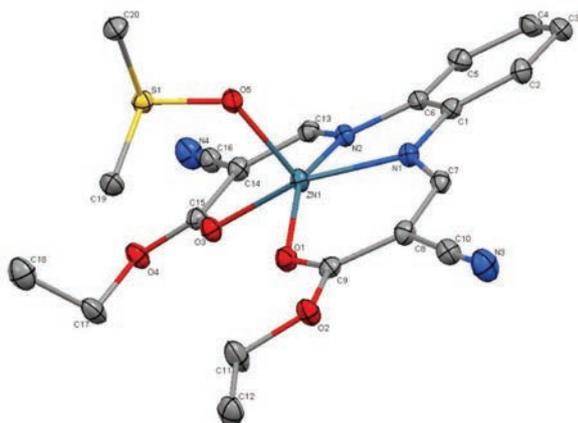
Fig. 1 Crystal structure of zinc complex **2**. (Crystallographic data of the structure have been deposited at the Cambridge Crystallographic Data base Centre CCDC; supplementary publication no. CCDC 954796.)

N_2O_2-ligand occupying the equatorial plane (Fig. 1, more details in ESI†). This structure is the first one involving zinc and a N_2O_2 ligand with amine and ester functions, while the bulk of the other documented Zn/N_2O_2 + L structures involve the more common salen/salophen-ligands (with phenol and aldimine functionalities).[9,10]

Catalytic tests

Using catalyst **2** for the conversion of propylene oxide (PO) with CO_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.[11,12] Ionic tetrabutyl ammonium salts are very active in our case. Especially Bu_4NI 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.[11,13] Plausibly, the conversion rates in the presence of chloride-containing cocatalysts were considerably lower. The neutral 4-(dimethyl-amino)-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).[14,15]

The variation of the reaction conditions (T, p, cat%, time) underlined the efficiency of the combination of zinc complex **2**/Bu_4NI. 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)

Table 1 Conversion of propylene oxide with CO_2 to propylene carbonate

Entry	Cat./Cocat.[a]	T (°C)	P (bar)	Cat conc[a] (mol%)	t (h)	Yield[b] (%)	TON	TOF (h^{-1})
1		80	50	0.2	20			
2	**2**/DMAP	80	50	0.2	20	**8%**	38	
3	**2**/MeIm	80	50	0.2	20	**6%**	27	
4	**2**/PPNCl	80	50	0.2	20	**3%**	16	
5	**2**/Bu_4NBr	80	50	0.2	20	**52%**	261	
6	**2**/Bu_4NCl	80	50	0.2	20	**21%**	106	
7	**2**/Bu_4NI	80	50	0.2	20	**99%**	493	
8	Fe N_2O_2/ [5,9]	80	50	0.2	20	**99%**	495	
9	Fe N_2O_2/ [5,9]	80	35	0.1	20	**69%**	690	
10	**2**/Bu_4NI	80	50	0.1	20	**97%**	966	48.3
11	**2**/Bu_4NI	80	50	0.01	20	**64%**	6357	
12	**2**/Bu_4NI	100	50	0.2	20	**99%**	496	
13	**2**/Bu_4NI	60	50	0.2	20	**98%**	490	
14	**2**/Bu_4NI	40	50	0.2	20	**93%**	446	
15	**2**/Bu_4NI	30	50	0.2	20	**58%**	288	
16	**2**/Bu_4NI	80	50	0.1	10	**95%**	954	95.4
17	**2**/Bu_4NI	80	50	0.1	3	**84%**	842	280.7
18	**2**/Bu_4NI	80	50	0.1	1	**74%**	744	744.0
19	**2**/Bu_4NI	80	2	0.2	20	**20%**[c]	100	
20	**2**/Bu_4NI	40	2	0.1	20	**63%**	604	
21	**2**/Bu_4NI	40	2	0.2	20	**88%**	439	

[a] Catalyst : cocatalyst 1 : 1. [b] Determined by subtracting the catalyst weight from the obtained product weight after removing epoxide remainders in vacuum and checking the purity with ^{1}H NMR. [c] Also contains polypropylene ether. Yield is estimated by ^{1}H NMR in benzene d_6 with an internal standard (tetrachloroethane).[5]

Table 2 Conversion of cyclohexene oxide with CO_2 to cyclohexene carbonate and poly(cyclohexene carbonate) (100% carbonate linkage)

Entry	Cat./Cocat.	Estimation by ^{1}H NMR[a]			Precipitated polymer[b]		
		CHC	PCHC	PCHC	T_g	M_n	PDI
1		0%	11%				
2	2/Bu$_4$NI	30%	15%				
3	2/Bu$_4$NBr	24%	3%				
4	2/Bu$_4$NCl	0%	33%	19%	84.0	3600	1.27
5	2/PPNCl	0.4%	58%	57%	89.4	7200	1.26
6[c]	Al N$_2$O$_2$ [6,9]/Bu$_4$NBr	1%	99%	97%	114.1	14 500	1.47

Reaction conditions: 80 °C, 50 bar, c(cat cocat) 1.0 mol%, 20 h. [a] Products were estimated using ^{1}H NMR in benzene d$_6$. [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.

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/Bu$_4$NI 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 CO_2 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 ^{1}H NMR, being pure alternating aliphatic poly(cyclohexene carbonates) (PCHC). As in the case of propylene oxide, catalyst 2 has to be used with a cocatalyst to display a notable catalytic activity. The nature of the cocatalyst has a great impact on the product spectrum: in agreement with the results obtained with propylene oxide, the cocatalysts with more nucleophilic anions (Bu$_4$NI and Bu$_4$NBr, entries 2, 3) lead to higher yields of cyclic carbonate, cyclohexene carbonate being however less favoured than propylene carbonate as expected from the literature.[16] The concurrently obtained polycarbonates could not be precipitated from the reaction mixture, compelling us to rely on IR and ^{1}H NMR data to evaluate the selectivity of the CO_2–epoxide coupling (see ESI† for spectra). Switching to cocatalysts with chloride as an anion, changed the product distribution and delivered PCHC as the major product. Traces of cyclic carbonates can be still noticed in the IR spectra (entry 5), an accurate integration of these traces of cyclic carbonate using ^{1}H NMR is however not easy.[9] The obtained copolymers were long enough to allow a separation using the usual dichloromethane–methanol precipitation.[17] According to the recorded glass transition temperatures (T_g), average molecular

weights (M_n) and polydispersity indexes (PDI), it appears that PPNCl (bis(triphenylphosphine)iminium chloride) is a tad better than tetra-n-butylammonium chloride (entry 5). An enhanced catalytic activity towards polycarbonate formation using PPNCl as a cocatalyst has already been reported by Darensbourg in the case of chromium salen complexes.[18] This is partly explained by PPNCl being highly hydrophobic while it is quite challenging to get Bu$_4$NCl completely anhydrous. Traces of water and consequently of 1,2-cyclohexane-diol, potential chain transfer agents in the copolymerization, may affect both the catalyst's efficiency and the nature of the polycarbonate. For the sake of comparison the related N$_2$O$_2$(malonate)–aluminium complex[6,9] is also listed in Table 2. In this particular case the use of Bu$_4$NBr as the best cocatalyst leads to the formation of pure aliphatic polycarbonates. As far as the formation of polycarbonates is concerned, the performance of the aluminium–N$_2$O$_2$(malonate) system is superior to the zinc–N$_2$O$_2$(cyano-acrylate) system. However, the easier synthesis, handling and storage of the air-stable zinc compounds combined with a high catalytic activity towards cyclic carbonates are significant advantages for the development of a durable supported catalyst.[19] In addition the possibility to gather reliable structural information for this particular class of N$_2$O$_2$-derivatives is also a significant advantage for future DFT studies aimed to understand the influence of ligand structure and cocatalyst on the course of the coupling reaction.

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 Bu$_4$NI and Bu$_4$NBr 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 Bu$_4$NCl) leads to the formation of pure alternating polycarbonates.

Acknowledgements

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