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# A Lewis acid $\beta$ -diiminato-zinc-complex as all-rounder for co- and terpolymerisation of various epoxides with carbon dioxide†

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A  $\beta$ -diiminato-zinc- $N(\text{SiMe}_3)_2$  complex (**1**) was synthesised and fully characterised, including an X-ray diffraction study. The activity of catalyst **1** towards the coupling reaction of  $\text{CO}_2$  and various epoxides, including propylene oxide (PO), cyclohexene oxide (CHO), styrene oxide (SO), limonene oxide (LO), octene oxide (OO) and epichlorohydrin (ECH), was investigated. Terpolymerisation of  $\text{CO}_2$ , PO and LO, as well as  $\text{CO}_2$ , CHO and PO, was successfully realised, resulting in polymers with adjustable glass transition temperatures and transparencies. Reaction conditions such as temperature, pressure and catalyst concentration were varied to find the optimal reaction values, especially regarding LO/ $\text{CO}_2$ . *In situ* IR experiments hinted that at 60 °C and a critical LO concentration, polymerisation and depolymerisation are in an equilibrium (ceiling effect). Pressurising catalyst **1** with carbon dioxide resulted in a dimeric catalyst (**2**) with a  $\text{OSiMe}_3$  group as a new initiator. Homopolymerisation of different epoxides was carried out in order to explain the reactivity concerning copolymerisation reaction of  $\text{CO}_2$  and epoxides.

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## Introduction

The chemical fixation of carbon dioxide for the preparation of cyclic- or polycarbonates has been targeted by many research groups to date.<sup>1–6</sup> Polycarbonates from renewable sources have the potential to replace petroleum-based plastics such as poly(propylene), poly(ethylene), polystyrene or bisphenol A carbonate. Until now, none of the current polycarbonates derived from carbon dioxide and epoxides (Fig. 1) display all of the desired polymer properties. Poly(propylene carbonate) (PPC), which is already produced in industry, is biocompatible and biodegradable. It can be used as a film due to its good barrier for  $\text{O}_2$  and water, it burns in air without emitting toxic materials and it has a long elongation at break. However, its glass transition temperature ( $T_g$ ) of 25–40 °C (body temperature) limits the range of its industrial applications.<sup>7,8</sup> In contrast, poly(cyclohexene carbonate) (PCHC) has a high  $T_g$  of ca. 120 °C, but its brittleness causes unfavourable mechanical properties. Terpolymerisation of different epoxides and  $\text{CO}_2$  is a promising strategy towards altering disadvantageous homopolymer properties.<sup>9–11</sup> It is still

challenging, as most complexes are specific for only one monomer. Besides, the majority of catalysts that are able to polymerise different epoxides are based on the toxic metals cobalt and chromium.<sup>9,11,12</sup> Apart from the production of typical polycarbonates like PPC or PCHC, fabrication of bio-based poly(limonene carbonate) (PLimC) has attracted much attention recently.<sup>13–20</sup> Limonene oxide (LO) is based on limonene, which is one of the most common terpenes in nature, found in the peel of many citrus fruits.<sup>21</sup> Elastic properties, water solubility, antibacterial characteristics or hydrophobicity can be introduced by post-modification of the double bond of the PLimC.<sup>19</sup> However, there are only a few catalysts reported in the literature which are active for this copolymerisation, as LO exhibits an internal,

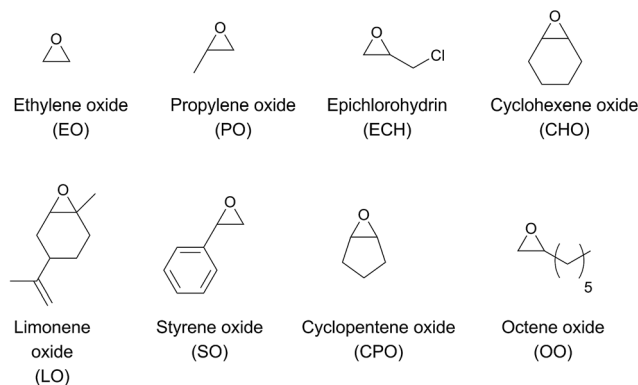


Fig. 1 Various epoxides for copolymerisation with carbon dioxide.

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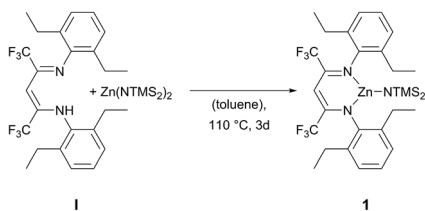
tri-substituted motif with a high kinetic barrier.<sup>14,15,17</sup> So far, turnover frequencies (TOFs) of the complexes are still low, and the reported catalysts are sensitive towards high epoxide-to-catalyst ratios.<sup>14,15</sup>  $\beta$ -diiminato-zinc (BDI-zinc) complexes exhibit the best activities, but are only able to copolymerise *trans*-LO.<sup>15,17</sup> Recently, a revised strategy for the synthesis of *trans*-enriched LO (84% *trans*) was published to avoid redundant *cis*-LO.<sup>13</sup> There is already an easy synthetic approach for a successful kinetic resolution with up to 98% de for both diastereomers.<sup>22</sup> We recently reported an activity enhancement of BDI-based zinc complexes regarding copolymerisation of CO<sub>2</sub> and cyclohexene oxide (CHO) by introducing electron-withdrawing groups.<sup>23,24</sup> Herein, we present the utilisation of a newly developed Lewis acid BDI-zinc complex for co- and terpolymerisation of CO<sub>2</sub> and an expanded set of epoxides, including the sterically demanding monomer LO.

## Results and discussion

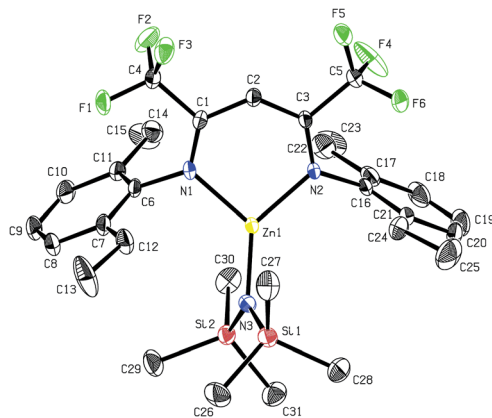
### Synthesis of $\beta$ -diiminato-zinc-NTMS<sub>2</sub> (1)

The ligand BDI<sup>CF<sub>3</sub></sup>-H(I) can be synthesised by a literature procedure in a condensation reaction with TiCl<sub>4</sub>, 2,6-diethyl-amine and 1,1,1,5,5,5-hexafluoroacetylacetone.<sup>25</sup> In order to obtain the corresponding complex (1), ligand I was stirred at 110 °C with 1.2 equivalents of *bis*[*bis*(trimethylsilyl)-amido]zinc in dry toluene for three days under argon atmosphere (Scheme 1).

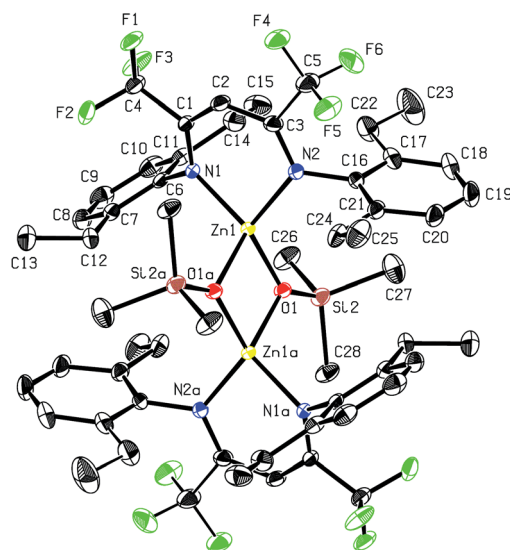
Recrystallisation from toluene at −35 °C afforded yellow crystals, which were suitable for single-crystal X-ray diffraction (SC-XRD). The molecular structure of catalyst 1 in the solid state is depicted in Fig. 2. The metal core adopts a trigonal-planar geometry with a Zn–N(SiMe<sub>3</sub>)<sub>2</sub> bond length of 1.869(2) Å. Compound 1 can be compared with a literature known <sup>1</sup>Pr-BDI<sup>CH<sub>3</sub></sup>-Zn–N(SiMe<sub>3</sub>)<sub>2</sub> complex (4), which bears methyl instead of trifluoromethyl groups in the pentane backbone and iso-propyl groups instead of ethyl groups at the aniline (Zn–N(SiMe<sub>3</sub>)<sub>2</sub>, 1.896(2) Å).<sup>26</sup> The Zn1–N1 (1.986(2) Å) and Zn1–N2 (1.967(2) Å) bonds differ slightly in their length, as the N(SiMe<sub>3</sub>)<sub>2</sub> ligand is marginally shifted to one side (C2, Zn1 and N3 are not strictly linear). Pressurising a solution of the catalyst in toluene with 40 bar CO<sub>2</sub> resulted in precipitation of a new dimeric catalyst [BDI<sup>CF<sub>3</sub></sup>-Zn- $\mu$ -OSiMe<sub>3</sub>]<sub>2</sub> (2). SC-XRD revealed the resulting structure of this compound, which is presented in Fig. 3. During this reaction (Scheme 2), CO<sub>2</sub> is inserted into the Zn1–N3 bond, and after migration of the trimethylsilyl group, trimethylsilyl isocyanate is released (the <sup>1</sup>H-NMR spectrum of the mother liquor is shown in Fig. S1†).<sup>27</sup>



**Scheme 1** Synthesis of  $\beta$ -diiminato-zinc-N(SiMe<sub>3</sub>)<sub>2</sub> 1 by reaction of BDI<sup>CF<sub>3</sub></sup> ligand I and the zinc precursor.



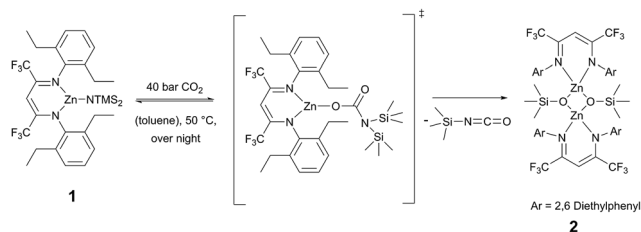
**Fig. 2** ORTEP style representation of 1 (hydrogen atoms omitted for clarity) with ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (deg): Zn1–N1 1.986(2), Zn1–N2 1.967(2), Zn1–N3 1.869(2), N1–Zn1–N2 97.11(8), N3–Zn1–N2 134.61(9), N3–Zn1–N1 128.11(9).



**Fig. 3** ORTEP style representation of 2 (hydrogen atoms omitted for clarity) with ellipsoids drawn at the 50% probability level. The complex features an intramolecular centre of inversion. Disordered groups are indicated by thin bonds. Selected bond lengths (Å) and bond angles (deg): Zn1–Zn2 2.9486(4), Zn1–N1 2.035(1), Zn1–N2 2.029(1), Zn1–O1 1.966(1), Zn1–O1A 2.019(1), N1–Zn1–N2 94.36(5), O1–Zn1–N2 120.97(5), O1–Zn1–N1 126.35(5), O1–Zn1–O1A 84.55(4).

Complex 2 is a dimeric catalyst having four electron withdrawing CF<sub>3</sub> groups in the ligand backbones. The solid state structure shows a siloxide-bridged dimer with a distorted tetrahedral geometry around each zinc centre. In comparison to 1 the Zn–N bond lengths of 2 are significantly elongated (Zn1–N1 = 2.035(1) Å, Zn1–N2 = 2.029(1) Å). The Zn–Zn distance of 2.9486(4) Å is very short, similar to a reported [BDI<sup>CH<sub>3</sub></sup>-Zn- $\mu$ -OSiMe<sub>3</sub>]<sub>2</sub> complex.<sup>27</sup> In contrast, pressurising a previously reported catalyst BDI<sup>CF<sub>3</sub></sup>-Zn-ethyl (3) with CO<sub>2</sub> at 50 °C overnight did not lead to the insertion of CO<sub>2</sub> (no reaction at all was observed).





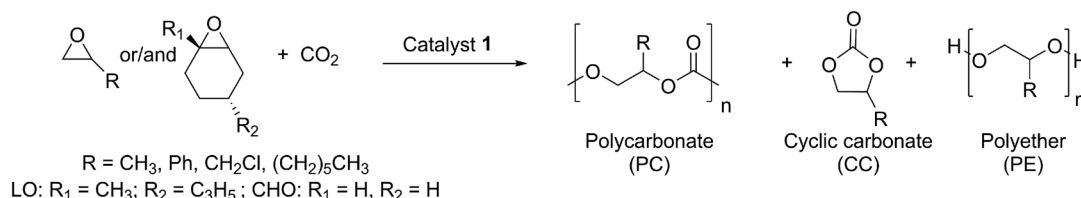
Scheme 2 Catalyst 2 is synthesized via pressurizing 1 with 40 bar CO<sub>2</sub> in toluene.

### Copolymerisation of epoxides and CO<sub>2</sub> with catalyst 1

After full characterisation of 1 by NMR spectroscopy, elemental analysis and SC-XRD, the compound was employed as a catalyst for copolymerisation experiments of CO<sub>2</sub> and epoxides (Table 1). There is a huge variety of epoxides and only selected examples were used within this work in order to show the catalyst's capacity. Previously, we reported about the activity of a BDI<sup>CF<sub>3</sub></sup>-Zn-ethyl catalyst (3) towards copolymerisation of CHO/CO<sub>2</sub>. PCHC with a TOF of 4800 h<sup>-1</sup>, 91% polycarbonate linkages and a molecular weight of 102 kg mol<sup>-1</sup> (PDI 1.3, bimodal) was achieved.<sup>24</sup> Catalyst 1 yielded 57% PCHC with good selectivity for carbonate linkages (93%) within 12.5 min (TOF 5520 h<sup>-1</sup>) under the same reaction conditions ([Cat] : [CHO] = 1 : 2000, 50 °C and 40 bar CO<sub>2</sub>). The resulting polymer was analysed by gel permeation chromatography (GPC), which showed a bimodal distribution curve and a molecular weight of 134 kDa with a PDI of 1.7. Especially regarding PCHC, this bimodality is often seen in the

literature and can be explained by the presence of residual water.<sup>28–30</sup> Another interesting monomer is propylene oxide (PO), as it is very cheap and can also be produced from CO<sub>2</sub>. It has one main drawback, as owing to a facile depolymerisation (backbiting), the formation of cyclic propylene carbonate is often observed. Catalyst 3 is not able to produce PPC (see further discussion below). In contrast, experiments (Table 1, entries 3–5) demonstrate that with catalyst 1, copolymerisation of PO and CO<sub>2</sub> is possible. At room temperature, a selectivity for PPC of up to 78% was achieved, whereas no formation of ether linkages was observed. PPC with a high molecular weight of 98 kg mol<sup>-1</sup> and a narrow PDI of 1.4 could be achieved using 0.1 mol% catalyst. Raising the temperature to 50 °C led to better activity, but almost exclusively, cyclic propylene carbonate was isolated. Furthermore, the catalyst was tested for styrene oxide (SO), epichlorohydrin (ECH), LO and octene oxide (OO). The coupling reaction of CO<sub>2</sub> and ECH at 40 °C led solely to the formation of cyclic ECH carbonate. At 20 °C, no reaction was observed. With regard to SO, there are only a few reports in the literature dealing with the coupling reaction of SO/CO<sub>2</sub>, and they are again mostly based on Co(III)-salen systems.<sup>31–34</sup> Complex 1 is indeed able to copolymerise SO and CO<sub>2</sub>, with a high epoxide-to-catalyst ratio, but only a moderate selectivity for polycarbonate of 66% (34% cyclic styrene carbonate). Furthermore, an *M<sub>n</sub>* of 19.6 kDa with a narrow PDI (1.3) was measured *via* GPC in tetrahydrofuran. Finally, even LO/CO<sub>2</sub> copolymerisation was realised with good selectivity for PLimC and moderate TOF (variation of the reaction conditions is summarised in Table 3). The excellent versatility of catalyst 1 was shown in terpolymerisation reactions with CHO/PO/CO<sub>2</sub> or LO/PO/CO<sub>2</sub>. High-molecular-

Table 1 Coupling reaction of CO<sub>2</sub> and epoxides with catalyst 1<sup>a</sup>



Entry	Epoxide	[Epoxide]: [[1]]	<i>p</i> [bar]	<i>T</i> [°C]	Time [h]	Yield [%]	TON <sup>b</sup>	TOF <sup>c</sup> [h <sup>-1</sup> ]	Selectivity (NMR) <sup>d</sup> [PC] : [CC] : [PE]	Terpolymer composition (NMR) <sup>e</sup> [PC] : [PPC] : [CC]	<i>M<sub>n</sub></i> (PDI) <sup>f,g</sup> [kg mol <sup>-1</sup> ]
1	CHO	2000	40	50	0.2	57	1150	5520	93 : 0 : 7	—	134 (1.7) <sup>g</sup>
2	CHO	4000	40	50	0.58	50	2010	3440	91 : 0 : 9	—	135 (1.4) <sup>g</sup>
3	PO <sup>h</sup>	1000	30	25	20	56	560	30	62 : 38 : 0	—	98 (1.4) <sup>f</sup>
4	PO <sup>h</sup>	1000	30	50	1	12	120	120	3 : 94 : 3	—	—
5	PO	500	30	25	3	32	160	53	78 : 22 : 0	—	21 (1.2) <sup>f</sup>
6	SO	1000	30	25	20	51	510	26	66 : 34 : 0	—	20 (1.3) <sup>g</sup>
7	OO	1000	40	40	24	92	920	38	33 : 66 : 0	—	107 (1.7) <sup>f</sup>
8	ECH	1000	30	40	16	44	440	28	0 : 100 : 0	—	—
9	LO	250	30	40	16	73	90	180	100 : 0 : 0	—	33 (1.9) <sup>f</sup>
10	LO/PO	250/600	30	25	6	40	330	55	98 : 2 : 0	51 : 47 : 2	95 (1.4) <sup>f</sup>
11	CHO/PO	500/500	30	25	14	65	650	46	99 : 1 : 0	59 : 40 : 1	272 (1.3) <sup>f</sup>

<sup>a</sup> Reaction scheme refers to copolymerisation of PO, SO, OO, ECH with CO<sub>2</sub> (PLimC, PCHC and terpolymers look different). <sup>b</sup> The turnover number (TON) is the ratio of the number of moles of epoxide consumed to the number of moles of catalyst. <sup>c</sup> TOF is TON/time. <sup>d</sup> [PC] : [CC] : [PE], assigned by the relative integrals of the signals for polycarbonate (PC), cyclic carbonate (CC) and polyether (PE). <sup>e</sup> [PC] : [PPC] : [CC], assigned by the relative signals for (a) entry 10: PLimC : PPC : cPC (b) entry 11: PCHC : PPC : cPC before precipitation. <sup>f</sup> Determined by GPC, calibrated with polystyrene standards in chloroform. <sup>g</sup> Determined by GPC, calibrated with polystyrene standards in thf. <sup>h</sup> 5.0 mL toluene.



weight polymers were produced, whereby the glass transition temperature could be varied from 39 °C (PPC/PLimC, Table 1, entry 10, Fig. S8†) to 50 °C (PPC/PCHC, Table 1, entry 11, Fig. S8†). UV-vis measurements showed that films of LO/PO/CO<sub>2</sub> terpolymer (0.70 mm thick) have a very good transmission of 95–99% in the range 400–800 nm (Fig. S9†). A film out of a CHO/PO/CO<sub>2</sub> terpolymer (0.13 mm thick) exhibits transmission of 80–90% in the range 400–800 nm (Fig. S9†). Further investigations are ongoing to examine the influence of different epoxide ratios on glass transition temperatures, transmissions and strain-stress behaviour.

### Ring-opening homopolymerisation of PO, CHO and LO

The copolymerisation experiments with different epoxides and CO<sub>2</sub> showed that catalyst **1** is very active for all tested monomers. On the other hand, catalyst **3** with a different initiator (ethyl) is only able to copolymerise CHO/CO<sub>2</sub> and is not active for PO/CO<sub>2</sub> or LO/CO<sub>2</sub>. SC-XRD revealed that complex **1** inserts CO<sub>2</sub> into the Zn–N bond in order to form the dinuclear complex **2**, whereas complex **3** did not show any reaction with CO<sub>2</sub>. However, the synthesis of **2** is slow, and only low conversion is observed.

To get more insight into the reaction mechanism, ring-opening homopolymerisation experiments with catalysts **1–3** and PO, CHO and LO were performed (Table 2). It was therefore found that CHO can be ring opened by complexes **1**, **2** and **3** (Table 2, entries 1, 4 and 7). In this case, there is no need for CO<sub>2</sub> in order to start the polymerisation. However, catalyst **3** shows only low conversion for formation of poly(cyclohexene oxide) due to a low initiator efficiency (Table 2, entry 3). In contrast to CHO, PO can only be slowly homopolymerised by catalyst **2**. The <sup>1</sup>H-NMR spectra showed that coordination of the epoxide to the respective catalyst occurs in all cases, as the signal of the initiation group is marginally shifted, but only catalyst **2** is able to ring open PO (Fig. S2–S4†). LO is also coordinated (<sup>1</sup>H-NMR spectra, Fig. S2–S4†), but apparently none of the initiation groups are able to attack the epoxide. All results indicate that the true active species during copolymerisation of CO<sub>2</sub> and epoxides with complex **1** is formed *in situ* in the reaction with CO<sub>2</sub> (Scheme 2, intermediate). Furthermore, in literature, it was

shown that acetate is a good initiator for the coupling reaction of CO<sub>2</sub>/LO, which resembles the *in situ* formed –OCONTMS<sub>2</sub> group.<sup>15</sup> As catalyst **3** is not able to insert CO<sub>2</sub>, PO and LO cannot be ring-opened, and no copolymerisation occurs.

### Variation of the reaction conditions of the coupling reaction of CO<sub>2</sub>/LO

Catalyst **1** was also tested for LO/CO<sub>2</sub> copolymerisation. Firstly, the reaction temperature was varied between 25 °C, 40 °C and 60 °C at an epoxide-to-catalyst ratio of 250 : 1 (0.4 mol%) and 30 bar. All experiments were conducted in an autoclave with *in situ* IR monitoring to follow the reaction progress (Fig. 4). Raising the temperature from 25 °C to 40 °C resulted in a higher TOF, but similar overall yields (full conversion was not achieved perhaps owing to the high viscosity of the polymer mixture). At 60 °C, catalyst **1** only yielded 17% PLimC. The *in situ* IR spectrum shows that after about 4 h, the carbonyl-stretching band of PLimC is not increasing anymore. Coates *et al.* reported very low conversions at 50 °C for their BDI–Zn catalyst owing to an axial attack at the stereogenic carbon centre of (1*R*,4*R*)-1-methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptane (*cis*-LO) at this temperature (formation of *trans*\*-PLimC, slow reaction due to steric hindrance).<sup>15</sup> The <sup>1</sup>H and <sup>13</sup>C-NMR spectra of our polymers showed that (1*S*,4*R*)-1-methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptane (*trans*-LO) is primarily attacked by the catalyst at the sterically less hindered C-atom (*trans*-PLimC) at all temperatures. If the *trans*-LO is opened at the most substituted carbon centre of the oxirane unit, inversion of the configuration leads to the formation of *cis*\*-PLimC. At higher temperatures, the attack at the stereogenic centre of *trans*-LO and *cis*-LO is more likely than at 25 °C (Table 3, entry 3, up to 5% *cis*\*-PLimC, 1% *trans*\*-PLimC). Decreasing the catalyst concentration to 0.2 mol% leads to a slow reaction after 4 h and a lower overall conversion (Table 3, entry 8, 46% yield). A yield of 3% *cis*\*-PLimC was determined, accompanied by low molecular masses and a broad PDI. Interestingly, the TOF could be increased in a solvent-free polymerisation using 50 bar CO<sub>2</sub> at

Table 2 Ring-opening homopolymerisation of PO, CHO and LO with complexes **1–3**<sup>a</sup>

Entry	Cat	Epoxide	[Epoxide] : [Cat]	Yield [%]	TON <sup>b</sup>
1	<b>1</b>	CHO	500	52	260
2	<b>1</b>	PO	500	0	0
3	<b>1</b>	LO	250	0	0
4	<b>2</b>	CHO	500	56	280
5	<b>2</b>	PO	500	5	25
6	<b>2</b>	LO	250	0	0
7	<b>3</b>	CHO	500	5	25
8	<b>3</b>	PO	500	0	0
9	<b>3</b>	LO	250	0	0

<sup>a</sup> All experiments were performed at room temperature (~23 °C) over 16 hours in neat epoxide. <sup>b</sup> The turnover number (TON) is the ratio of the number of moles of epoxide consumed to the number of moles of catalyst.

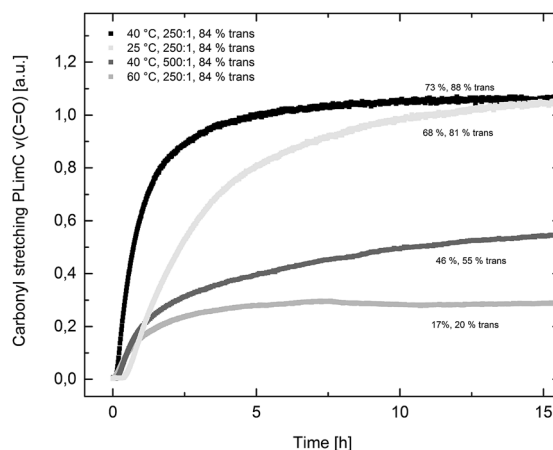
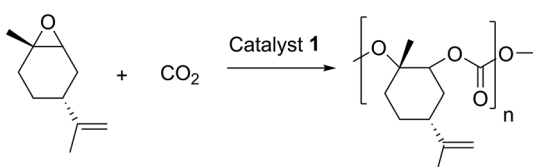


Fig. 4 The formation of PLimC against time (carbonyl stretching  $\nu(\text{C}=\text{O})$  in a.u. against time in h). Yields are given concerning 30.5 mmol *cis*-/*trans* LO and regarding the actual amount of *trans*-LO (x% *trans*).





Table 3 Copolymerisation of limonene oxide and carbon dioxide with catalyst **1** under different reaction conditions<sup>a</sup>

											
Entry	[LO] : [1]	% <i>trans</i> LO	V (tol) [mL]	Pressure [bar]	Temperature [°C]	Time [h]	Yield [%]	Yield <i>trans</i> -LO [%]	<i>trans</i> / <i>cis</i> */ <i>trans</i> * <sup>b</sup> [%]	TOF <sup>c,d</sup>	<i>M</i> <sub>n</sub> (PDI) <sup>e</sup> [g mol <sup>-1</sup> ]
1	250	84	2	30	25	16	68	81	100 : 0 : 0	60 <sup>c</sup>	62.000 (1.7)
2	250	84	2	30	40	16	73	88	99.6 : 0.3 : 0	180 <sup>c</sup>	32.500 (1.9)
3	250	84	2	30	60	16	17	20	94 : 5 : 1	40 <sup>c</sup>	4.300 (1.6)
4	250	54	2	30	40	16	51	94	96 : 2 : 2	110 <sup>c</sup>	10.000 (1.3)
5	250	54	2	30	60	16	11	21	95 : 3 : 2	30 <sup>c</sup>	7.200 (1.7)
6	250	>99	2	30	40	6.5	59	59	100 : 0 : 0	120 <sup>c</sup>	145.300 (1.3)
7	250	>99	2	30	60	16	26	26	97 : 3 : 0	110 <sup>c</sup>	56.100 (2.5)
8	500	84	2	30	40	16	46	55	97 : 3 : 0	110 <sup>c</sup>	19.000 (2.5)
9	500	84	0	30	40	3	35	42	99 : 1 : 0	60 <sup>d</sup>	24.000 (1.9)
10	500	84	0	30	60	0.66	20	24	95 : 5 : 0	130 <sup>d</sup>	4.900 (1.9)
11	500	84	0	30	80	3	0	0	—	—	—
12	500	84	0	10	60	3	0	0	—	—	—
13	500	84	0	50	60	0.5	30	36	98 : 2 : 0	310 <sup>d</sup>	12.800 (1.8)
14	500	84	0	50	60	16	40	50	96 : 4 : 0	15 <sup>d</sup>	9.500 (2.6)
15	1000	84	0	50	60	3.5	13	16	95 : 5 : 0	40 <sup>d</sup>	6.000 (2.1)

<sup>a</sup> Volume (LO) = 5.0 mL (30.5 mmol). <sup>b</sup> Selectivity for *trans*/*cis*\*/*trans*\*-PLimC was determined by <sup>13</sup>C NMR spectroscopy (ESI). <sup>c</sup> *In situ* TOF is determined by a calibration curve S5, intensity  $\nu(\text{C}=\text{O})$  vs.  $n(\text{PLimC})$ . <sup>d</sup> TOF is defined as TON/time. <sup>e</sup> Determined by GPC, calibrated with polystyrene standards in chloroform.

0.2 mol% catalyst and 60 °C (Table 3, entry 14). A maximum TOF of 310 h<sup>-1</sup> was achieved, which is the highest reported TOF for the formation of PLimC so far.<sup>13</sup> However, once again, only up to 40% yield was reached after 16 h (Table 3, entry 14). We considered *cis*-LO as a catalyst quencher, as this monomer stays untouched at low temperatures (<sup>13</sup>C-NMR spectrum, Fig. 5c), whereas at 60 °C, the formation of approximately 1% *trans*\*-PLimC was observed (Table 3, entry 3). Therefore, the amount of *cis*-LO was first varied from <1% to 10% and 46% at 40 °C (30.5 mmol, 5.0 mL LO with different composition, 2 mL toluene, 30 bar). In these cases, no deactivation of the catalyst was observed (Fig. S7†). With a higher amount of *cis*-LO, the overall yield for *trans*-PLimC was even increased owing to a good solubility of the polymer in the residual *cis*-LO (lower viscosity) and a higher catalyst concentration with regard to *trans*-LO. The highest reported molecular masses of 145 kg mol<sup>-1</sup> with a small PDI of 1.3 were achieved using >99% *trans*-LO at 40 °C and 30 bar CO<sub>2</sub>. Applying the same conditions at 60 °C, the catalyst yielded again only 11–26% PLimC (Table 3, entries 3, 5 and 7). Using >99% *trans*-LO, the IR monitoring of the reaction showed that the intensity of the carbonyl-stretching band of PLimC increases only very slightly after 2 h (Fig. S6†). Thus, *cis*-LO could be excluded as a catalyst poison. Another possibility is deactivation of complex **1** via the double bond of *cis*-/*trans*-LO. Zn- $\pi$  interactions are rare, but are reported in the literature.<sup>35,36</sup> In order to verify the influence of the double bond, LO (54% *trans*) was hydrated with PtO<sub>2</sub>/H<sub>2</sub>, and the resulting menthene oxide was copolymerised with CO<sub>2</sub> at 30 bar, 0.4 mol% catalyst **1**

and 25 °C or 60 °C (ESI Table S1, Fig. S10 and S11†). An initiation time of about 40 min was observed at 25 °C, and high-molecular-weight *trans*-polymenthene carbonate (PMenC) (*M*<sub>n</sub> = 149 kDa, PDI 1.2) was produced. At 60 °C and over 16 h, only 4% regioirregular PMenC (Fig. S11†) was generated (*M*<sub>n</sub> = 5.6 kDa, PDI 1.3), which indicates that even in the absence of a double bond, complex **1** is deactivated. In summary, *cis*-LO as well as the double bond of LO could be excluded as catalyst

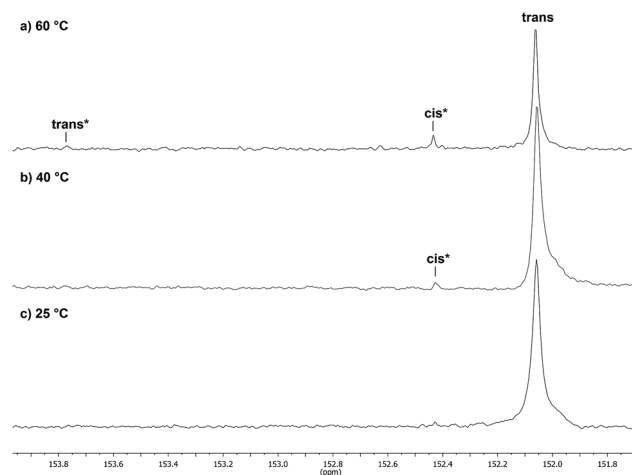


Fig. 5 <sup>13</sup>C-NMR spectra (expansion 153.9–151.6 ppm) of PLimC, produced at different polymerisation temperatures: (a) 60 °C (Table 3, entry 3), (b) 40 °C (Table 3, entry 2) and (c) 25 °C (Table 3, entry 1).



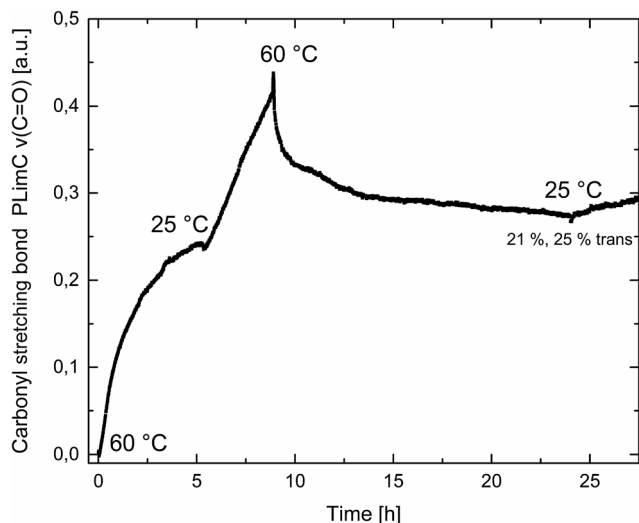


Fig. 6 Formation of the carbonyl stretching of PLimC in a.u. against time in h at different temperatures. Overall conversion was 21%, and regarding *trans*-LO, 25%.

poisons. A third possible explanation for all the aforementioned observations is that the ceiling temperature of PLimC is around 60 °C at an LO concentration of about 3.5 mol L<sup>-1</sup>. Every polymerisation is an equilibrium reaction, whereby the balance can be shifted towards the formation of polymer or the reverse by varying temperature, pressure and concentration of the monomer.<sup>37</sup> At 60 °C, a critical concentration of LO is achieved during the polymerisation, where the reverse reaction is just as fast as the polymer formation itself. We do not detect the formation of cyclic limonene carbonate by *in situ* IR spectroscopy and <sup>1</sup>H-NMR, so the reverse reaction is the release of CO<sub>2</sub> and LO (and not the usual backbiting). An experiment in the autoclave with *in situ* IR monitoring was performed at 60 °C, 30 bar and a catalyst loading of 0.4 mol% (Fig. 6). After the signal of the carbonyl stretching of PLimC approached a plateau, the temperature was decreased to 25 °C. The polymer signal started to increase linearly as soon as the right temperature was achieved. After a few hours, a temperature of 60 °C was applied again, and the carbonyl stretching of PLimC decreased to the original level from the beginning of the cycle. That means that depolymerisation occurred until the critical LO concentration (ca. 3.5 mol L<sup>-1</sup>) was achieved. In a last step, the temperature was set to 25 °C, which led again to an increasing polymer signal, though with a clearly decreased slope. Therefore, besides this thermodynamic control, there should be, in addition, kinetic aspects which have to be considered, e.g. deactivation of the catalyst by traces of contaminants in LO.

## Conclusion

In summary, we introduced a versatile Lewis acid BDI-based zinc catalyst with an N(SiMe<sub>3</sub>)<sub>2</sub> initiation group for copolymerisation of many different epoxides and CO<sub>2</sub>. We found out that pressurising the catalyst with CO<sub>2</sub> leads to the insertion of the latter and a subsequent release of trimethylsilyl isocyanate.

Ring-opening studies of PO, CHO and LO indicate that the real active species is primarily the *in situ* generated carbonato-intermediate. Even terpolymerisation experiments with different monomers were successful, as they resulted in polymers with tuneable properties such as *T<sub>g</sub>* or transparency. In addition, copolymerisation reactions with LO/CO<sub>2</sub> were performed, which showed that catalyst 1 is the most active catalyst for the formation of PLimC reported so far. However, at a temperature of 60 °C, conversions were much lower than expected. *cis*-LO and the double bond of LO could be excluded as catalyst poisons. *In situ* IR experiments showed that at 60 °C, depolymerisation is in an equilibrium with polymer formation at a critical LO concentration.

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## Notes and references

- 1 G. W. Coates and D. R. Moore, *Angew. Chem., Int. Ed.*, 2004, **43**, 6618–6639.
- 2 G. Trott, P. K. Saini and C. K. Williams, *Philos. Trans. R. Soc. London, Ser. A*, 2016, **374**, 20150085.
- 3 B. Rieger, A. Künkel and G. W. Coates, *Synthetic Biodegradable Polymers*, Springer, Berlin, Heidelberg, Germany, 2012.
- 4 M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann and F. E. Kühn, *Angew. Chem., Int. Ed.*, 2011, **50**, 8510–8537.
- 5 X.-B. Lu and D. J. Darensbourg, *Chem. Soc. Rev.*, 2012, **41**, 1462–1484.
- 6 S. Klaus, M. W. Lehenmeier, C. E. Anderson and B. Rieger, *Coord. Chem. Rev.*, 2011, **255**, 1460–1479.
- 7 G. A. Luinstra and E. Borchardt, *Adv. Polym. Sci.*, 2012, **245**, 29–48.
- 8 G. A. Luinstra and E. Borchardt, *Polym. Rev.*, 2008, **48**, 192–219.
- 9 L. Shi, X.-B. Lu, R. Zhang, X.-J. Peng, C.-Q. Zhang, J.-F. Li and X.-M. Peng, *Macromolecules*, 2006, **39**, 5679–5685.
- 10 D. J. Darensbourg, R. R. Poland and A. L. Strickland, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 127–133.
- 11 W.-M. Ren, X. Zhang, Y. Liu, J.-F. Li, H. Wang and X.-B. Lu, *Macromolecules*, 2010, **43**, 1396–1402.
- 12 J. E. Seong, S. J. Na, A. Cyriac, B.-W. Kim and B. Y. Lee, *Macromolecules*, 2010, **43**, 903–908.
- 13 O. Hauenstein, M. Reiter, S. Agarwal, B. Rieger and A. Greiner, *Green Chem.*, 2016, **18**, 760–770.
- 14 L. Peña Carrodegua, J. González-Fabra, F. Castro-Gómez, C. Bo and A. W. Kleij, *Chem.-Eur. J.*, 2015, **21**, 6115–6122.
- 15 C. M. Byrne, S. D. Allen, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2004, **126**, 11404–11405.



- 16 F. Auriemma, C. De Rosa, M. R. Di Caprio, R. Di Girolamo and G. W. Coates, *Macromolecules*, 2015, **48**, 2534–2550.
- 17 F. Auriemma, C. De Rosa, M. R. Di Caprio, R. Di Girolamo, W. C. Ellis and G. W. Coates, *Angew. Chem., Int. Ed.*, 2015, **54**, 1215–1218.
- 18 C. Li, R. J. Sablong and C. E. Koning, *Angew. Chem., Int. Ed.*, 2016, **55**, 11572–11576.
- 19 O. Hauenstein, S. Agarwal and A. Greiner, *Nat. Commun.*, 2016, **7**, 11862.
- 20 C. Martín and A. W. Kleij, *Macromolecules*, 2016, **49**, 6285–6295.
- 21 R. Ciriminna, M. Lomeli-Rodriguez, P. Demma Cara, J. A. Lopez-Sanchez and M. Pagliaro, *Chem. Commun.*, 2014, **50**, 15288–15296.
- 22 D. Steiner, L. Ivison, C. T. Goralski, R. B. Appell, J. R. Gojkovic and B. Singaram, *Tetrahedron: Asymmetry*, 2002, **13**, 2359–2363.
- 23 S. Kissling, M. W. Lehenmeier, P. T. Altenbuchner, A. Kronast, M. Reiter, P. Deglmann, U. B. Seemann and B. Rieger, *Chem. Commun.*, 2015, **51**, 4579–4582.
- 24 M. Reiter, A. Kronast, S. Kissling and B. Rieger, *ACS Macro Lett.*, 2016, **5**, 419–423.
- 25 A. Kronast, M. Reiter, P. T. Altenbuchner, C. Jandl, A. Pöthig and B. Rieger, *Organometallics*, 2016, **35**, 681–685.
- 26 M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 8738–8749.
- 27 D. R. Moore, M. Cheng, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2003, **125**, 11911–11924.
- 28 M. R. Kember and C. K. Williams, *J. Am. Chem. Soc.*, 2012, **134**, 15676–15679.
- 29 K. Nakano, T. Kamada and K. Nozaki, *Angew. Chem., Int. Ed.*, 2006, **45**, 7274–7277.
- 30 H. Sugimoto, H. Ohtsuka and S. Inoue, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 4172–4186.
- 31 G.-P. Wu, S.-H. Wei, X.-B. Lu, W.-M. Ren and D. J. Darensbourg, *Macromolecules*, 2010, **43**, 9202–9204.
- 32 R.-J. Wei, X.-H. Zhang, B.-Y. Du, X.-K. Sun, Z.-Q. Fan and G.-R. Qi, *Macromolecules*, 2013, **46**, 3693–3697.
- 33 Y. Dienes, W. Leitner, M. G. J. Muller, W. K. Offermans, T. Reier, A. Reinholdt, T. E. Weirich and T. E. Muller, *Green Chem.*, 2012, **14**, 1168–1177.
- 34 G.-P. Wu, S.-H. Wei, W.-M. Ren, X.-B. Lu, B. Li, Y.-P. Zu and D. J. Darensbourg, *Energy Environ. Sci.*, 2011, **4**, 5084–5092.
- 35 A. Wooten, P. J. Carroll, A. G. Maestri and P. J. Walsh, *J. Am. Chem. Soc.*, 2006, **128**, 4624–4631.
- 36 R. Benn, H. Grondy, H. Lehmkuhl, H. Nehl, K. Angermund and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1279–1280.
- 37 G. Odian, *Principles of Polymerization*, John Wiley & Sons, New York, 1981.

