Copolymerization

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Flexibly Tethered Dinuclear Zinc Complexes: A Solution to the Entropy Problem in CO_2/Epoxide Copolymerization Catalysis?**

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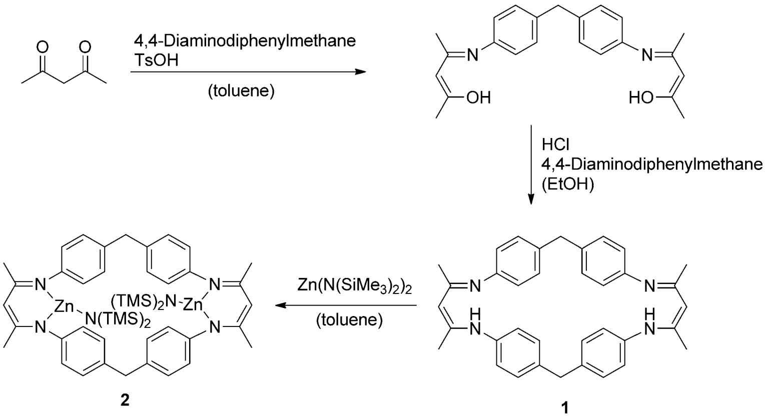
World-wide research activities over the last decade have demonstrated that carbon dioxide is a valuable carbon source for a series of chemical products.[1–8] One very promising class of products is aliphatic polycarbonates, synthesized by the reaction of carbon dioxide and epoxides. These polymers show interesting properties, as they are biodegradable, highly transparent, UV stable, and have a high Young's modulus.[9–12] Latest research even led to isotactic poly(cyclohexene carbonates), opening a route to semi-crystalline thermoplastic materials.[13]

Despite the fact that aliphatic polycarbonates were already introduced 40 years ago by Inoue et al., the development of an economic production process is still hampered by the availability of efficient catalysts. The main focus of numerous publications in this field was based on a dinuclear catalysts, which accommodate the epoxide ring opening and a CO_2 insertion in a single molecule.[8,10,12,14–21] Zinc as a catalytically active species has tremendous advantages compared to other transition metals. It is an economic, ecofriendly element, and its ions are colorless. For that reason since 2003 a variety of dinuclear zinc catalysts has been developed. However, most of the reported structures suffer from poor solubility or low polymerization activity.[16,22–30]

One major breakthrough aside from zinc phenoxides developed by Darensbourg is the synthesis of β-diketiminato (BDI) zinc complexes by Coates et al.[21,31–41] For these highly active catalysts the mechanism involving a dimetallic intermediate was unambiguously demonstrated. Kinetic investigations using in situ IR spectroscopy showed that the rate-determining step is the ring opening of the epoxide.[21] Williams et al. also reported the incorporation of the epoxide as rate determining for their rigid dinuclear zinc catalysts.[20] This implies that at typical process conditions an increase in CO_2 concentration does not automatically enhance polymerization activity.

The concept presented herein also focuses on dinuclear complexes. However, two BDI zinc units are connected by a flexible tether. This helps to overcome the entropically disfavored aggregation of two individual complex molecules in dilute solutions in a way that the rate-determining step is even shifted from ring opening to CO_2 insertion.

The new macrocyclic ligand **1** (Scheme 1) was prepared in a two-step synthesis in which each step involves the condensation of 4,4-diaminodiphenylmethane with acetylacetone. A highly efficient synthesis of the desired complex **2** was carried out in toluene with bis[bis(trimethylsilyl)amido]zinc at 90 °C.



Scheme 1. Synthesis of the dinuclear catalyst **2**. TMS = trimethylsilyl, TsOH = 4-methyl benzenesulfonic acid.

The dinuclear character of the complex was confirmed by elemental analysis and NMR spectroscopy. The ^1H NMR spectrum shows broadened resonance signals for the trimethylsilyl groups at 25 °C. Upon heating the sample to 80 °C the broad signals coalescence, which we attribute to a hindered rotation of the $N(TMS)_2$ groups caused by steric repulsion. The other resonance signals of the complex are narrow and confirm the symmetric configuration of the molecule (Figure S1 in the Supporting Information). The catalyst was tested in the copolymerization of cyclohexene oxide and carbon dioxide under various reaction conditions.

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For a detailed understanding of this catalyst system kinetic studies were performed with online ATR (attenuated total reflection) IR measurements. For these measurements it is important to confirm that the reaction mixture is homogeneous and the IR signal increases linearly with increasing amount of polycarbonate.[7,8] The homogeneity of the reaction mixture in the IR autoclave was demonstrated by an experiment without stirring. Therefore, covering of the probe by precipitation of copolymer during the reaction can be excluded (Figure S5).[42] The IR signal grows linearly with increasing amount of polycarbonate. The kinetic order with respect to catalyst was obtained by performing the copolymerization at different catalyst concentrations. By plotting the initial rate against the catalyst concentration in a double logarithmic scale the first-order dependence in catalyst is obtained (Figure 1).

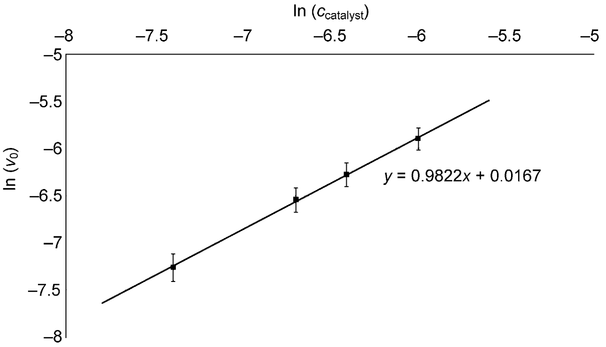


Figure 1. Determination of the order with respect to catalyst.

With this confirmation of the expected catalyst concentration dependence, kinetic investigations concerning the CO_2 pressure and the cyclohexene oxide concentration were undertaken. Measurements for different pressures were carried out in the same manner as the assignment of the order with respect to catalyst. At first, the CO_2 uptake in the cyclohexene oxide/toluene mixtures was studied, and a clearly linear increase of the IR signal with increasing pressure was found (Figure S8). With constant catalyst and cyclohexene oxide concentration the order with respect to carbon dioxide was determined to be one in the range of 5–25 bar CO_2 pressure. For 25–45 bar the order with respect to CO_2 concentration changes surprisingly from one to zero (Figure 2).

The assignment of the order with respect to cyclohexene oxide was performed at two different pressures 10 and 30 bar. The determination of the order with respect to epoxide at 10 bar reveals a value of zero and a reaction order of one at 30 bar (Figure 3).

These results lead to the rate laws given in Equations (1) and (2) where CHO = cyclohexene oxide:

$$r = k\,[\mathrm{CHO}]^0\,[\mathrm{CO_2}]^1\,[\mathrm{Catalyst}]^1 \qquad 5\text{–}25\ \mathrm{bar\ CO_2} \tag{1}$$

$$r = k\,[\mathrm{CHO}]^1\,[\mathrm{CO_2}]^0\,[\mathrm{Catalyst}]^1 \qquad 25\text{–}45\ \mathrm{bar\ CO_2} \tag{2}$$

The different aspects of the rate laws are discussed in the following parts, beginning with the first order with respect to catalyst. The groundbreaking work of Coates et al. showed that two mononuclear complexes and consequently two metal centers are necessary for chain propagation.[21] Therefore, the first order dependence on catalyst is in accordance to the dinuclearity of the described catalyst. Kinetic measurements on other zinc catalysts show that the rate-determining step for the copolymerization is the ring opening of the epoxide.[20,21] Thus, herein the first zinc-based epoxide/CO_2 copolymerization catalyst is reported which shifts the rate-determining step from ring opening of the epoxide to carbon dioxide insertion at technically relevant CO_2 pressures (Scheme 2 and Figure S9). Considering the first order dependence with respect to epoxide of all the other catalysts, this suggests that the flexible tether between the two zinc centers accelerates the cooperative ring-opening step in an unprecedented manner and to an extent that a pressure depenency of the rate equations occurs. This assumption is strongly supported by the synthesis of a similar complex **3** without such a flexible tether which exhibits very low activities for this copolymerization under identical conditions (Table S5).

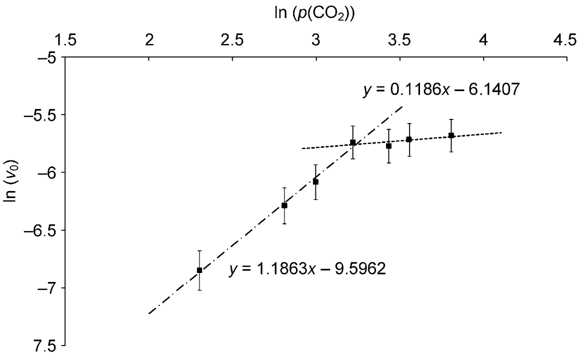


Figure 2. Rate dependence on carbon dioxide pressure.

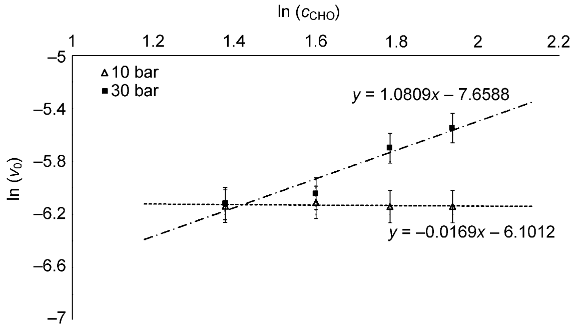
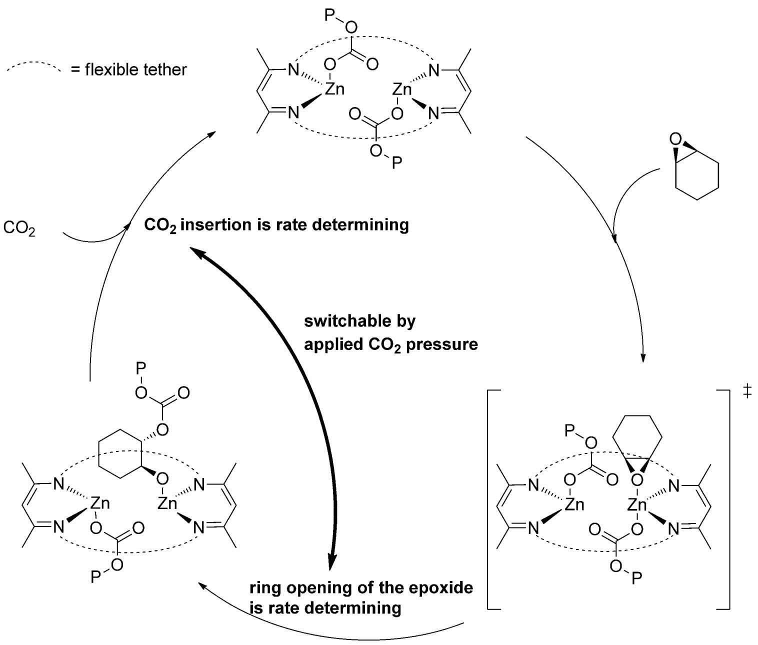


Figure 3. Order with respect to cyclohexene oxide.

This shift in the rate-determining step and the involvement of two cooperating zinc centers is further supported by quantum chemical computations, which were performed to rationalize the above findings. Calculations were performed at the B3-LYP/def2-TZVP||BP86/SV(P) level of theory, involving enthalpic and entropic corrections and a treatment of solvation by COSMO-RS as described elsewhere.[43] As solvent, toluene was used and a temperature of 100 °C as well as CO_2 pressures of 5 and 50 bar. The motivation for the method applied and details on enthalpic and entropic



Scheme 2. Proposed mechanism for the copolymerization with the pressure dependence of the rate determining step.

correction terms can be found in the Supporting Information. As starting point of the catalytic cycle, a κ^2,κ^2-dicarbonato complex was chosen, assuming that catalyst activation can and will readily take place at both sides of the plane made up by the ligand and the two-coordinated zinc atoms. From this species, the reaction is expected to proceed by coordination of epoxide, epoxide ring opening to form an alkoxide, and subsequent addition of this coordinated alkoxide to CO$_2$ (i.e. CO$_2$ insertion). Computed results for this reactive pathway are summarized in Figure 4. The catalytic cycle given does not contain all the intermediates involved in the reaction mechanism; however, further intermediates, for example, from dissociative ligand exchange were found to be not relevant for overall reaction kinetics (Figure S15). From the dicarbonato starting point **I**, creation of a free coordination site and epoxide coordination, leading to **II**, is exothermic, but not favorable with respect to Gibbs free energy for entropic reasons. The subsequent epoxide ring-opening transition state **TS(a)** is around 50 kJ mol^{-1} higher in enthalpy H than **I**, which should correspond

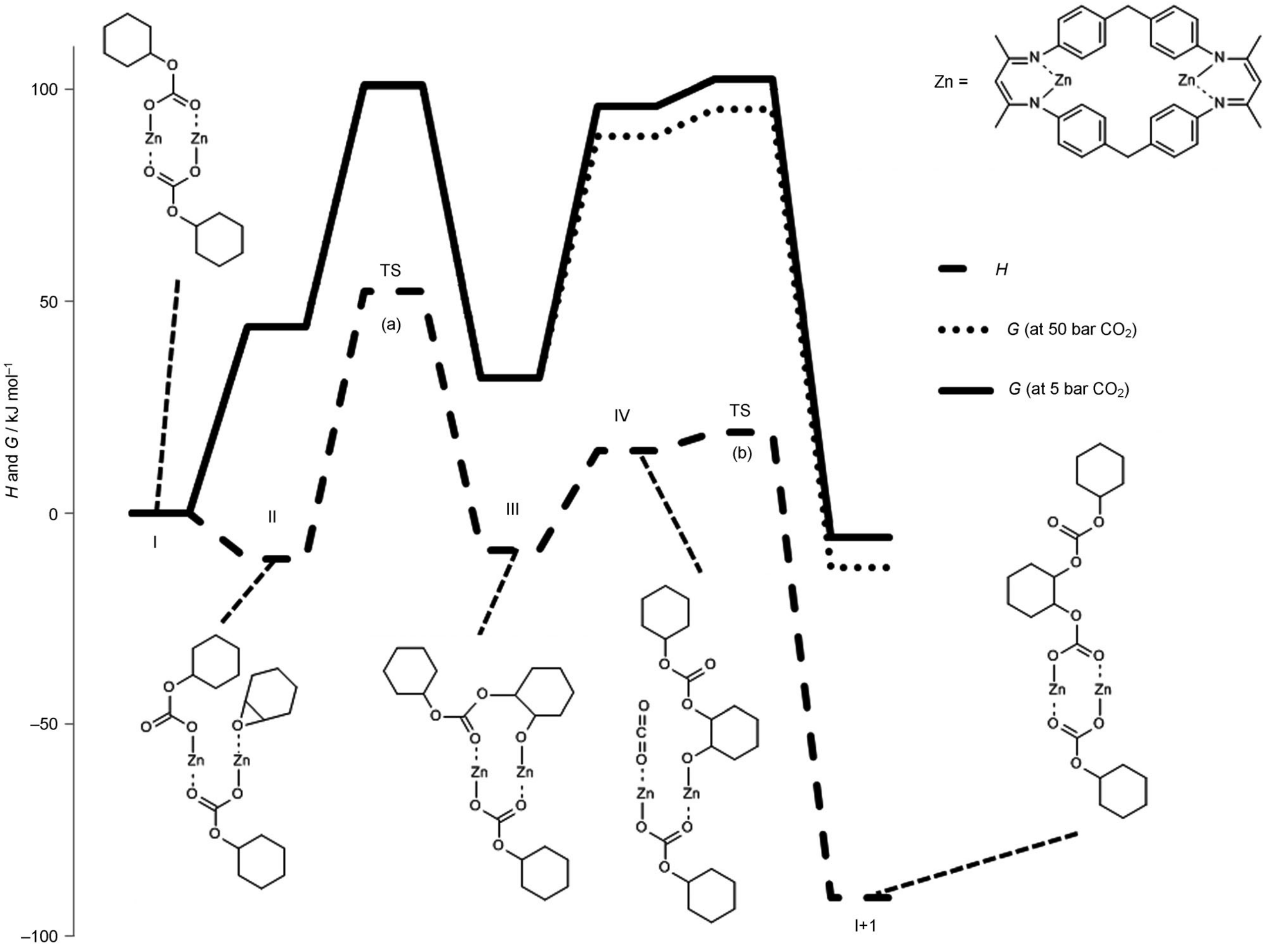


Figure 4. Enthalpy and Gibbs free energy profile for copolymerization catalyzed by **2** at 100 °C and a CO$_2$ pressures of 5 and 50 bar.

more or less to E_a in case of an Arrhenius evaluation of temperature dependent reaction rates, whereas the overall Gibbs free energy G to overcome for epoxide ring opening is around 100 kJ mol^{-1}. The immediately resulting bridged alkoxide species **III** is computed to be about as stable as **II**. Another rather stable alkoxide species (see Supporting Information) which has a μ^2-oxo bridge could be identified, but needs no further consideration owing to a higher relative G if compared to **I** and **III**. Addition of CO_2 to **III** leads to **IV**, which by a nucleophilic attack of the alkoxide at the carbonyl carbon atom, **TS(b)**, regenerates the propagated carbonato species **I** + **1**. Altogether, all the alkoxide species are significantly higher in G than **I**, therefore it is concluded that, independent of the rate-limiting step, the resting state is this dicarbonato species. Thus, for the incorporation of CO_2, the effective activation barriers have to be calculated with respect to **I**, this gives a computed H which suggests an E_a of around 20 kJ mol^{-1}, whereas the relative barrier with respect to G is again around 100 kJ mol^{-1} and depends on the applied CO_2 pressure. This striking similarity in the computed G value of both potentially highest lying transition states means that both transition states are similarly difficult to overcome (considering potential sources of error from the quantum chemical energy method as well as the solvation treatment), which is in line with the observed change in rate-limiting step upon variation of the CO_2 pressure: Whereas in the first part of the catalytic cycle CO_2 is not involved (**TS(a)**), increasing or decreasing the CO_2 pressure will shift the second (**TS(b)**) part downwards or upward, respectively. For high CO_2 pressures as high as the 50 bar considered in Figure 4, the epoxide ring opening **TS(a)** with its G_a of 101.0 kJ mol^{-1} is the highest point of the G profile compared to the G_a of 95.3 kJ mol^{-1} for the CO_2 insertion **TS(b)**; at lower CO_2 pressure (e.g. 5 bar), alkoxides are formed in a pre-equilibrium and undergo the rate-limiting CO_2 insertion, with for example, a G_a of 102.4 kJ mol^{-1} for **TS(b)** (Figure 4). The point where **TS(b)** is identical to the G_a of 101.0 kJ mol^{-1} of **TS(a)** is computed to be at a CO_2 pressure of around 8 bar, which is somewhat below the experimental 25 bar where both elementary reactions are "equally rate limiting"; at 25 bar, a G_a of 97.4 kJ mol^{-1} is obtained for **TS(b)**. This means however still a remarkably good agreement between experiment and theory considering typical errors of quantum chemical calculations for larger molecules in solution.

Kinetic studies at various temperatures were performed to further probe this mechanistic picture (Figure S16–S19). Experimental activation energies at 10 and 30 bar are found to be 8.8 and 35.9 kJ mol^{-1}, respectively. The computationally estimated values demonstrate the same trend. For low pressure (5 bar) the CO_2 insertion step is rate limiting with an activation energy of 19.2 kJ mol^{-1}, at higher pressure (50 bar) the epoxide ring opening becomes rate limiting with 52.3 kJ mol^{-1}. At a first glance, it appears surprising that elementary steps with such dissimilar activation energies can both be rate limiting. However, this is a consequence of Gibbs free activation energies depending on both activation enthalpies and activation entropies. As the resting state is in all cases the dicarbonato complex **I**, epoxide ring opening is a bimolecular reaction, that is, the incorporation of one solution species into the catalyst-bound polymer chain. On the other hand, CO_2 addition is effectively a trimolecular reaction, which consumes both one liquid epoxide and one gaseous CO_2. Consequently, the Gibbs free energy G for epoxide ring opening is higher than the corresponding enthalpy H (around 50 kJ mol^{-1}), but the difference between G and H for CO_2 insertion is even larger (around 80 kJ mol^{-1}). This, of course means that Arrhenius prefactors are significantly smaller for CO_2 insertion than for epoxide ring opening (for the measured E_a, a ratio of around 5000 in prefactors would be required at 100 °C to obtain similar rate coefficients at standard concentrations of all reactants).

The flexibility of the tether between the two β-diketiminato zinc centers is also supported by the calculations: Whereas for the bis[bis(trimethylsilyl)amido] precursor complex a Zn–Zn distance of 7.77 Å is computed, all the Zn–Zn distances within the actual catalytic cycle are significantly smaller but also exhibit a variation of more than 1 Å (the following distances are computed for the presented intermediates and transition states: **I** 4.50 Å, **II** 5.66 Å, **TS(a)** 5.31 Å, **III** 5.29 Å, **IV** 5.40 Å and **TS(b)** 4.92 Å).

It can be assumed that the accessibility of such a large range of Zn–Zn distances allows every transition state to adopt optimal structures and thus avoids additional barriers from catalyst rigidity, which means that the entropic benefit from not having to group two β-diketiminato zinc units together is fully exploited. The acceleration of the epoxide ring-opening step leads to the high copolymerization activities of the catalyst (Table 1).

With decreasing catalyst loading the activity slightly increases, which can be attributed to better diffusion (Table 1, entries 1–3). The dependence of the activity on CO_2 pressure is also documented (entries 3–6). The results for the selectivity for polycarbonate over cyclic carbonate are in accordance with those in the literature.[12,21,39] The selectivity increases with higher CO_2 pressure. The catalyst shows an unusual temperature dependence. The temperature of 100 °C seems to be the optimum with regard to polymerization activity and selectivity. The decreased activity at 120 °C could be explained by catalyst decomposition and a higher probability for side reactions (Table 1, entry 7). This catalyst exhibits a turnover frequency (TOF) of 9130 h^{-1} at 100 °C and 40 bar CO_2 pressure, a result of a good balance in activation barriers for the two potentially rate-determining steps.

In summary we report the first dinuclear zinc catalyst which shows a shift in the rate-determining step from ring opening of the epoxide to carbon dioxide insertion for the copolymerization of cyclohexene oxide and carbon dioxide. The reason for this behavior is the similarity of the activation barriers of the ring opening and insertion reactions, which is achieved by linking the two active centers with a flexible tether. These attributes lead to very high activities for the copolymerization reaction. To achieve even higher activities, according to our study, an additional decrease of the activation energy of the ring-opening step is necessary. The match between experimental and theoretical results delivers a tool for further catalyst development. Currently, modification of these catalysts is under investigation.

Table 1: Copolymerization of carbon dioxide and cyclohexene oxide with catalyst **2**.

	T [°C]	$p(CO_2)$ [bar]	TON[b]	TOF[c]	% poly-carbonate[d]	Conversion [%]
1	100	10	628[e]	1255[e]	99	62.8
2	100	10	1649	4946	98	41.2
3	100	10	1750[f]	5249[f]	98	21.9
4	100	5	1194	3581	97	29.9
5	100	20	2529	7587	>99	63.2
6	100	40	4015	9130	>99	
7	120	10	1190	1785	92	29.8
8	80	14	1251[k]	5003[k]	99	31
9	80	14	9440[g]	2860[g]	79[g]	18.9
10	100	10	127[h]	127[h]	0[h]	3.2

[a] Copolymerizations were conducted in a preheated Parr reactor for 20 min at a catalyst loading of catalyst/epoxide of 1:4000 in a toluene/cyclohexene oxide mixture (1:1 v/v) (unless otherwise stated). [b] The turnover number (TON) is calculated by the number of mole of consumed epoxide divided by the mole of catalyst. [c] The turnover frequency is calculated as TOF = TON/reaction period. [d] Assigned by the relative integrals of the signals at $\delta = 4.65$ (polycarbonate) and $\delta = 4$–4.08 ppm (cyclic carbonate). [e] Catalyst/epoxide 1/1000, 30 min reaction time in neat epoxide, not preheated. [f] Catalyst/epoxide 1:8000. [g] Catalyst as prepared by Lee et al. copolymerization in neat cyclohexene oxide for 3.3 h.[27] [h] $[Zn(N(TMS)_2)_2]$ was used in neat cyclohexene oxide as catalyst. [k] Neat cyclohexene oxide, 15 min reaction time.

Experimental Section

The synthesis of the ligand and the complexes are described in the Supporting Information.

Catalyst **2** (24.0 mg, 0.025 mmol, 0.1 mol %) was dissolved in cyclohexene oxide (2.5 mL, 24.8 mmol, 1.0 equiv). The autoclave was pressurized with 10 bar carbon dioxide and heated to 100 °C. The reaction was terminated after 20 min by the addition of methanol (1.0 mL) and teh reaction mixture dissolved in methylene chloride. The organic phase was washed with HCl (1M) and dried with Na_2SO_4. After evaporation of the solvent the poly(carbonate) was dried in an oven to constant weight.

^{1}H NMR (300 MHz, $CDCl_3$, 292 K): $\delta = 4.58$ (s, 2 H), 1.30–2.04 ppm (m, 8 H).

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[1] M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kuhn, *Angew. Chem.* **2011**, *123*, 8662 – 8690; *Angew. Chem. Int. Ed.* **2011**, *50*, 8510 – 8537.
[2] D. J. Darensbourg, *Chem. Rev.* **2007**, *107*, 2388 – 2410.
[3] G. W. Coates, D. R. Moore, *Angew. Chem.* **2004**, *116*, 6784 – 6806; *Angew. Chem. Int. Ed.* **2004**, *43*, 6618 – 6639.
[4] M. R. Kember, A. Buchard, C. K. Williams, *Chem. Commun.* **2011**, *47*, 141 – 163.
[5] S. Klaus, M. W. Lehenmeier, C. E. Anderson, B. Rieger, *Coord. Chem. Rev.* **2011**, *255*, 1460 – 1479.
[6] C. Bruckmeier, M. W. Lehenmeier, R. Reichardt, S. Vagin, B. Rieger, *Organometallics* **2010**, *29*, 2199 – 2202.
[7] S. I. Vagin, R. Reichardt, S. Klaus, B. Rieger, *J. Am. Chem. Soc.* **2010**, *132*, 14367 – 14369.
[8] S. Klaus, S. I. Vagin, M. W. Lehenmeier, P. Deglmann, A. K. Brym, B. Rieger, *Macromolecules* **2011**, *44*, 9508 – 9516.
[9] M. W. Lehenmeier, C. Bruckmeier, S. Klaus, J. E. Dengler, P. Deglmann, A.-K. Ott, B. Rieger, *Chem. Eur. J.* **2011**, *17*, 8858 – 8869.
[10] S. Klaus, M. W. Lehenmeier, E. Herdtweck, P. Deglmann, A. K. Ott, B. Rieger, *J. Am. Chem. Soc.* **2011**, *133*, 13151 – 13161.
[11] G. A. Luinstra, *Polym. Rev.* **2008**, *48*, 192 – 219.
[12] G. A. Luinstra, G. R. Haas, F. Molnar, V. Bernhart, R. Eberhardt, B. Rieger, *Chem. Eur. J.* **2005**, *11*, 6298 – 6314.
[13] G.-P. Wu, W.-M. Ren, Y. Luo, B. Li, W. Z. Zhang, X.-B. Lu, *J. Am. Chem. Soc.* **2012**, *134*, 5682 – 5688.
[14] a) R. Eberhardt, M. Allmendinger, G. A. Luinstra, B. Rieger, *Organometallics* **2003**, *22*, 211 – 214; b) S. Inoue, H. Koinuma, T. Tsuruta, *Makromol. Chem.* **1969**, *130*, 210 – 220.
[15] J. E. Dengler, M. W. Lehenmeier, S. Klaus, C. E. Anderson, E. Herdtweck, B. Rieger, *Eur. J. Inorg. Chem.* **2011**, 336 – 343.
[16] M. R. Kember, P. D. Knight, P. T. Reung, C. K. Williams, *Angew. Chem.* **2009**, *121*, 949 – 951; *Angew. Chem. Int. Ed.* **2009**, *48*, 931 – 933.
[17] M. R. Kember, A. J. P. White, C. K. Williams, *Inorg. Chem.* **2009**, *48*, 9535 – 9542.
[18] M. R. Kember, A. J. P. White, C. K. Williams, *Macromolecules* **2010**, *43*, 2291 – 2298.
[19] A. Buchard, M. R. Kember, K. G. Sandeman, C. K. Williams, *Chem. Commun.* **2011**, *47*, 212 – 214.
[20] F. Jutz, A. Buchard, M. R. Kember, S. B. Fredriksen, C. K. Williams, *J. Am. Chem. Soc.* **2011**, *133*, 17395 – 17405.
[21] D. R. Moore, M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2003**, *125*, 11911 – 11924.
[22] S. D. Allen, D. R. Moore, E. B. Lobkovsky, G. W. Coates, *J. Organomet. Chem.* **2003**, *683*, 137 – 148.
[23] K. Nozaki, K. Nakano, T. Hiyama, *J. Am. Chem. Soc.* **1999**, *121*, 11008 – 11009.
[24] K. Nakano, K. Nozaki, T. Hiyama, *J. Am. Chem. Soc.* **2003**, *125*, 5501 – 5510.
[25] K. Nakano, T. Hiyama, K. Nozaki, *Chem. Commun.* **2005**, 1871 – 1873.
[26] Y. Xiao, Z. Wang, K. Ding, *Chem. Eur. J.* **2005**, *11*, 3668 – 3678.
[27] T. Bok, H. Yun, B. Y. Lee, *Inorg. Chem.* **2006**, *45*, 4228 – 4237.
[28] B. Y. Lee, H. Y. Kwon, S. Y. Lee, S. J. Na, S. Han, H. Yun, H. Lee, Y.-W. Park, *J. Am. Chem. Soc.* **2005**, *127*, 3031 – 3037.
[29] M. F. Pilz, C. Limberg, B. B. Lazarov, K. C. Hultzsch, B. Ziemer, *Organometallics* **2007**, *26*, 3668 – 3676.
[30] D. F. Piesik, S. Range, S. Harder, *Organometallics* **2008**, *27*, 6178 – 6187.
[31] D. J. Darensbourg, M. W. Holtcamp, *Macromolecules* **1995**, *28*, 7577 – 7579.
[32] D. J. Darensbourg, S. A. Niezgoda, J. D. Draper, J. H. Reibenspies, *J. Am. Chem. Soc.* **1998**, *120*, 4690 – 4698.
[33] D. J. Darensbourg, M. W. Holtcamp, G. E. Struck, M. S. Zimmer, S. A. Niezgoda, P. Rainey, J. B. Robertson, J. D. Draper, J. H. Reibenspies, *J. Am. Chem. Soc.* **1999**, *121*, 107 – 116.
[34] D. J. Darensbourg, J. R. Wildeson, J. C. Yarbrough, J. H. Reibenspies, *J. Am. Chem. Soc.* **2000**, *122*, 12487 – 12496.
[35] D. J. Darensbourg, P. Rainey, J. C. Yarbrough, *Inorg. Chem.* **2001**, *40*, 986 – 993.

[36] M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **1998**, *120*, 11018 – 11019.

[37] M. Cheng, N. A. Darling, E. B. Lobkovsky, G. W. Coates, *Chem. Commun.* **2000**, 2007 – 2008.

[38] M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 8738 – 8749.

[39] S. D. Allen, D. R. Moore, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2002**, *124*, 14284 – 14285.

[40] D. R. Moore, M. Cheng, E. B. Lobkovsky, G. W. Coates, *Angew. Chem.* **2002**, *114*, 2711 – 2714; *Angew. Chem. Int. Ed.* **2002**, *41*, 2599 – 2602.

[41] R. Duchateau, W. J. van Meerendonk, L. Yajjou, B. B. P. Staal, C. E. Koning, G.-J. M. Gruter, *Macromolecules* **2006**, *39*, 7900 – 7908.

[42] D. J. Darensbourg, J. L. Rodgers, R. M. Mackiewicz, A. L. Phelps, *Catal. Today* **2004**, *98*, 485 – 492.

[43] P. Deglmann, I. Müller, F. Becker, A. Schäfer, K.-D. Hungenberg, H. Weiß, *Macromol. React. Eng.* **2009**, *3*, 469 – 515.