Homogeneous Catalysis

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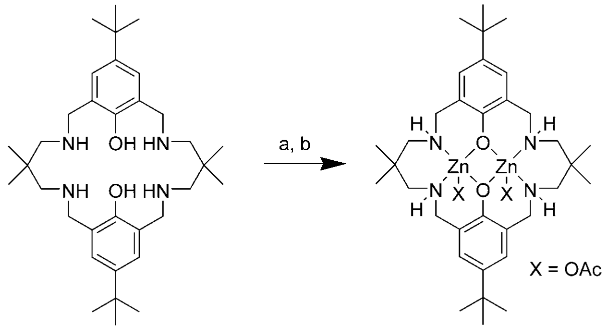
Highly Active Dizinc Catalyst for the Copolymerization of Carbon Dioxide and Cyclohexene Oxide at One Atmosphere Pressure**

*Michael R. Kember, Paul D. Knight, Palarp T. R. Reung, and Charlotte K. Williams**

A novel dizinc complex having a macrocyclic ancillary ligand shows remarkable activity at only one atmosphere of CO_2 for the copolymerization of CO_2 and cyclohexene oxide.

Carbon dioxide is an attractive reagent for synthetic chemistry as it is abundant, inexpensive, of low toxicity, and is the waste product of many chemical processes. The copolymerization of carbon dioxide and epoxides, known for several decades, is a particularly promising route to activate and use CO_2 as a renewable C-1 source.[1–5] Furthermore, if cyclohexene oxide is used, the resulting copolymer has a high glass transition temperature and tensile strength, but it is also degradable.[6] The first report of this type of copolymerization came from Inoue et al. in 1969, and they used diethyl zinc and alcohols to produce poly(propylene carbonate), albeit with very low turnover numbers (TONs).[7] Subsequently several research groups developed more active and controlled catalysts, and notable for their activity are the zinc phenoxide,[8–10] zinc β-diiminate,[11–17] and chromium(III)– or cobalt(III)–salen complexes.[18–20] The zinc β-diiminate complexes show very high turnover frequencies (TOFs), as well as excellent control for the copolymerization of CO_2 and cyclohexene oxide.[13] Recent mechanistic studies by Coates and co-workers suggest that the most effective β-diiminate complexes are loosely associated dimers under the polymerization conditions.[14] This proposal has led to the deliberate preparation of various dimetallic zinc catalysts,[21–25] and among these dizinc catalysts, the anilido aniline complexes show particularly high TONs and TOFs because they can operate at low catalyst loadings.[22,24] However, all of the known high activity catalysts require substantial (> 7 atm) pressures of carbon dioxide, which significantly increases the overall energy requirement of the process. Although catalysts which operate at only one atmosphere of CO_2 are known,[14,21,23,26,27] so far the best reported TON was 20 and the highest TOF was 3.3 h^{-1}.[21]

We report the preparation of a dimetallic zinc complex (Scheme 1) having a macrocyclic ancillary ligand, which shows very high activity for the copolymerization of cyclohexene oxide and carbon dioxide under mild pressures. The macrocyclic ligand H_2L^1 was prepared in two steps with 84% overall yield from commercial reagents (see the Supporting Information) by using an adaptation of a synthetic route described previously.[28] The dimetallic zinc complex, $[L^1Zn_2(OAc)_2]$ was synthesized by the deprotonation of H_2L^1 using potassium hydride, and subsequent reaction with zinc acetate. The complex was isolated as a white solid in 70% yield (Scheme 1). The stoichiometry of the complex was confirmed by elemental analysis, which was in agreement with the calculated values, and the identification of a fragment peak in the FAB mass spectrum for the molecular ion less an acetate group. The ^1H NMR spectrum at 25 °C shows broadened resonances, consistent with several diastereoisomers being present, which are fluxional on the NMR timescale. When the sample was heated to 110 °C coalescence was observed (see Figure S1 in the Supporting Information). A single resonance was observed for the aromatic protons and the signal for the NH groups was a broadened resonance at $\delta = 4.78$ ppm. The methylene groups are diastereotopic, therefore four broadened resonances were observed from $\delta = 3.32$–2.46 ppm, each with an integral corresponding to 4H. The signals for the *tert*-butyl groups and the methyl group of the acetate resonate as singlets with integrals corresponding to 18H and 6H, respectively. The methyl groups on the ligand backbone are also diastereotopic and are observed as two singlets, each with a relative integral corresponding to 6H.



H_2L^1 $[L^1Zn_2(OAc)_2]$

Scheme 1. The synthesis of the dizinc complex $[L^1Zn_2(OAc)_2]$. Reagents and conditions: a) KH, THF, −78 °C→RT, 1 h; b) $Zn(OAc)_2$, THF, RT, 16 h.

The complex was tested at low pressures for the copolymerization of carbon dioxide and cyclohexene oxide (Table 1). Thus, at only one atmosphere of CO_2, 80–100 °C, and a 0.1 mol% catalyst loading, poly(cyclohexene carbonate) was produced with a TON in the range of 430–530 and a TOF in the range of 18–25 h^{-1} (Table 1, entries 1–3). There are very few catalysts that are effective at such a low pressure,[14,21,23,26,27] the most active of which is a dizinc

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[*] M. R. Kember, Dr. P. D. Knight, P. T. R. Reung, Dr. C. K. Williams
Department of Chemistry
Imperial College London, London (UK)
E-mail: c.k.williams@imperial.ac.uk

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Table 1: The copolymerization of carbon dioxide and cyclohexene oxide, catalyzed by [$L^1Zn_2(OAc)_2$].[a]

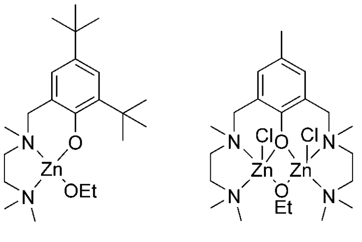
Entry	T [°C]	$p(CO_2)$ [atm]	TON[b]	TOF[c] [h^{-1}]	% carbonate[d]	% polycarbonate[e]	M_n[f]	PDI[f]
1	80	1	439	18	>99	96	6200	1.19
2	90	1	567	24	>99	95	6500	1.21
3	100	1	527	25	>99	94	7360	1.21
4	100	10	838	38	>99	96	7570	1.20
5[g]	100	10	3350	140	>99	95	14100[i]	1.03
6[h]	100	1	585	25	>99	96	3070	1.21
7 Ref. [21]	60	1	20	3.3	>99	N/A	19200	1.56
8 Ref. [11]	50	7	494	247	90	N/A	31000	1.10
9 Ref. [9]	80	55	365	8	>99	N/A	42000	6.00

[a] The copolymerizations were conducted in a Schlenk tube for 20–24 h, at a loading of [$L^1Zn_2(OAc)_2$]/cyclohexene oxide of 1:1000 (unless otherwise stated), or in a Parr reactor at 10 atm for 24 h (entries 4,5). [b] The turn over number (TON) = number of moles of cyclohexene oxide consumed/number of moles of [$L^1Zn_2(OAc)_2$]. [c] The turn over frequency (TOF) = TON/reaction period. [d] Determined by the relative integrals of the signals at $\delta = 3.45$ (polyether) and $\delta = 4.65$ ppm (polycarbonate). [e] Assigned by the relative integrals of the signals at $\delta = 4.65$ (polycarbonate) and $\delta =$ 4-4.08 ppm (cyclic carbonate). [f] Determined by SEC in THF, using narrow M_w polystyrene standards. [g] Carried out at a loading of [$L^1Zn_2(OAc)_2$]/cyclohexene oxide of 1:10 000. [h] Used unpurified (wet) cyclohexene oxide and the catalyst was handled in air. [i] A bimodal peak was observed with M_n of 14100 and 6600.[31] N/A = not applicable.

complex (Table 1, entry 7).[21] However, compared to this known catalyst, [$L^1Zn_2(OAc)_2$] has a TON which is 35 times greater and a TOF which is 5 times greater that those of the reported catalyst, albeit at a slightly higher temperature. The polymer produced has exceptionally good fidelity of carbonate repeat units, and ether linkages were not detected (see Figure S2 in the Supporting Information). There was also a small amount ($<6\%$) of cyclic carbonate, the yield of which increased slightly with increasing temperature because the polymerization is an equilibrium reaction and poly(cyclohexene carbonate) has a low ceiling temperature.[29,30] [$L^1Zn_2(OAc)_2$] displays comparable activity to the β-diiminate zinc or bis(phenoxide) zinc catalysts (Table 1, entries 8 and 9), but only at a fraction of the pressure of carbon dioxide (1/7 and 1/55 respectively). The high activity of [$L^1Zn_2(OAc)_2$] coupled with its ability to react at very low CO_2 pressure significantly improves the economical and environmental impacts of the copolymerization. When the pressure of CO_2 was increased (Table 1, entry 4), the TON and TOF increased to 838 and 38 h^{-1}, respectively. When the catalyst loading with reduced to 0.01 mol % (Table 1, entry 5) the TON and TOF increased to 3350 and 140 h^{-1}, respectively. Whereas the TOFs are not exceptional, the TONs are remarkably high, exceeding those obtained with the reported compounds (Table 1, entries 7–9) because the current catalyst is very tolerant and robust. Catalyst [$L^1Zn_2(OAc)_2$] is still active after 24 hours of reaction and at loadings of 0.01 mol %. It is also stable in air as evidenced by the comparable TONs and TOFs, which were obtained for polymerizations at 1 atm of CO_2 when [$L^1Zn_2(OAc)_2$] was handled in air and used with unpurified (i.e. wet) cyclohexene oxide (Table 1, entry 6), relative to running the reaction in an anaerobic environment (Table 1, entry 3). Such air stability has not previously been reported for any zinc catalyst, but it is advantageous for ease of use.

The polymerizations were well-controlled, giving polycarbonate with a narrow polydispersity index (PDI; Table 1). Monitoring the copolymerization shows there is a linear relationship between the molecular weight and percentage conversion (see Figure S3 in the Supporting Information), which is also a good indicator of controlled polymerization. The molecular weights for all the polycarbonates were, however, significantly lower than the expected values (based on the TON and the relative molecular mass (RMM) of the repeat unit). In fact this is a general phenomenon for most known catalysts, which show much lower than expected molecular weights because of chain transfer reactions.[8,9,11,12,14–17,19–25,29,30] The catalyst [$L^1Zn_2(OAc)_2$] has two initiating groups (two acetate groups) and is therefore expected to show molecular weights that are approximately half of those obtained with conventional catalysts (Table 1, entries 7 and 8), and this is indeed observed (Table 1, entries 1–5).[32] There is still considerable debate in the literature about the nature and source of the chain transfer agents,[17] however, for [$L^1Zn_2(OAc)_2$] it is apparent that water (in the unpurified cyclohexene oxide) is an efficient chain transfer agent and lowers the molecular weight of the polycarbonate (Table 1, entry 6 versus entry 3). The copolymer produced by using anaerobic conditions and purified cyclohexene oxide (Table 1, entry 3) was analyzed by MALDI-TOF mass spectrometry (see Figure S4 in the Supporting Information). The MALDI-TOF mass spectrum showed the expected series of peaks with an acetyl end group as well as series resulting from cyclopentyl and hydroxy end groups, the latter being at much lower molecular weight. Van Meerendonk and co-workers[17] have also observed these end groups using both the β-diiminate zinc and bis(phenoxide) zinc catalysts (Table 1, entry 8 and 9), and Xiao et al have observed similar end groups using the dimetallic zinc catalysts (Table 1, entry 7).[21,23]

It was of interest to establish whether the dimetallic core of the current catalyst was responsible for its high activity. A monometallic analogue complex, [L^2ZnOEt] (Figure 1), had previously been reported as a highly active lactide polymerization catalyst.[33] However, when this species was tested for CO_2/cyclohexene oxide copolymerization it was completely inactive and no polymer was produced. Also notable was that the dimetallic complex derived from an "open" analogue of the macrocyclic ligand, [$L^3Zn_2Cl_2OEt$] (Figure 1), which had shown good lactide polymerization activity,[34] was also inactive for CO_2/cyclohexene oxide copolymerization.[35] The most active known catalyst which operates at 1 atm (Table 1, entry 7) also has a closely related "open" ligand geometry to [$L^3Zn_2Cl_2OEt$] and shows substantially lower activity than [$L^1Zn_2(OAc)_2$].[21] We therefore attribute the remarkable activity of the current catalyst to both its dimetallic core and the macrocyclic ligand environment.



$[L^2ZnOEt]$ $[L^3Zn_2Cl_2OEt]$

Figure 1. Structures of $[L^2ZnOEt]$ and $[L^3Zn_2Cl_2OEt]$.

In conclusion, a novel macrocyclic dizinc complex exhibits excellent activity for the copolymerization of cyclohexene oxide and carbon dioxide at just one atmosphere of carbon dioxide. It shows an activity comparable to the most active species reported in the literature, but operates at a fraction of the pressure of carbon dioxide. It is also remarkably tolerant and robust.

Experimental Section

The syntheses of H_2L^1 and polymerization conditions are described in the Supporting Information.

Synthesis of $[L^1Zn_2(OAc)_2]$: H_2L^1 (0.40 g, 0.72 mmol) was dissolved in dry THF (10 mL) and transferred into a Schlenk tube containing KH (0.04 g, 1.08 mmol), and then cooled to −78 °C under nitrogen. This suspension was warmed to room temperature and then stirred for 1 hour. The excess KH was filtered off and the solution was transferred to a Schlenk tube containing $Zn(OAc)_2$ (0.27 g, 1.48 mmol). The reaction was stirred for 16 h, after which the THF was removed in vacuo, and the product taken up in dry CH_2Cl_2 (10 mL). This mixture was then filtered and the CH_2Cl_2 removed in vacuo to yield the title compound as a white powder (0.40 g, 70 %).

Found: C, 56.91; H, 7.46; N, 6.92 %; $C_{38}H_{60}N_4O_2Zn_2$ requires: C, 57.07; H, 7.56; N, 7.01 %; (400 MHz, $[D_2]$TCE, 383 K): $\delta_H = 7.00$ (s, 4 H, ArH), 4.78 (br s, 4 H, NH), 3.32 (br d, 4 H, CH_2), 2.95 (br s, 4 H, CH_2), 2.84 (br s, 4 H, CH_2) 2.46 (br s, ≈4 H, CH_2), 2.08 (s, ≈6 H, OAc), 1.35 (s, 18 H, $ArCCH_3$), 1.29 (s, 6 H, CH_2CCH_3), 1.05 ppm (s, 6 H, CH_2CCH_3); (400 MHz, $[D_2]$TCE, 383 K): $\delta_C = 174.7$, 159.5 (br), 139.5 (br), 127.4, 124.4, 63.2, 56.3, 33.5, 31.4, 27.9, 21.1 ppm and 20.7; m/z (FAB) 739 ($[M-OAc]^+$, 100 %).

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[31] The MALDI-TOF spectrum (see Figure S5 in the Supporting Information) of this sample also showed a bimodal distribution having the higher molecular weight peaks for the cyclopentyl end-capped polymer and the lower molecular weight peaks for the cyclohexyl/cyclohexenyl and water end-capped polymers. Such end groups (see references [17, 22, and 23]) and bimodality/broad molecular weight distributions (see references [15, 22, and 28]) have been frequently observed by other groups.
[32] The molecular weights are not precisely one half those obtained in the literature because of differences in the size-exclusion chromatography instruments, columns, and calibration methods. The molecular weight obtained using the known catalyst in entry 9 of Table 1 is discounted because of the large PDI value.
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