ORGANOMETALLICS

Solvent Dependence of the Structure of Ethylzinc Acetate and Its Application in CO₂/Epoxide Copolymerization

Katherine L. Orchard, Jonathan E. Harris, Andrew J. P. White, Milo S. P. Shaffer,* and Charlotte K. Williams*

Department of Chemistry, Imperial College London, Exhibition Road, London SW7 2AZ, U.K.

Supporting Information

ABSTRACT: NMR and single-crystal X-ray diffraction experiments indicate that the ligand stoichiometry of the complexes formed from the reaction between zinc bis(acetate) and diethylzinc depends on the nature of the solvent (coordinating vs noncoordinating) and that the strength of the donor interaction of a coordinating solvent (THF vs pyridine) affects the nuclearity of the complex's repeat unit in the solid state. The complexes are active catalysts for the copolymerization of cyclohexene oxide and CO_2 , under mild conditions.



rganozinc compounds were one of the earliest classes of organometallic compounds; indeed Frankland reported the preparation of diethylzinc as early as 1848.^{1,2} In the centuries that have followed, heteroleptic alkyl zinc reagents (RZnX, where X = halide, alkoxide, aryloxide, carboxylate, amide, etc.) have become established as useful reagents in organic synthesis,^{3,4} perhaps most well-known in palladium/nickel-catalyzed Negishi cross-coupling reactions or in addition reactions with carbonyl compounds; $^{5-10}$ they are also used as catalysts, for example in epoxide homopolymerization or the copolymerization of epox-ides and CO_2^{11-16} and as precursors for the preparation of ZnO.¹⁷⁻²⁹ The most widely studied are alkylzinc alkoxides, which form dimers ($[RZn(\mu-OR')]_2$), tetramers ($[RZn(\mu_3-$ OR']₄ "cubes"), and heptameric species ([$Zn_7(\mu_3 - OR')_8(R)_6$]) depending on the nature of the ligand, the dialkyl zinc:alcohol ratio, and the solution concentration. $^{30-32}$

In comparison, the structures and solution behavior of alkylzinc carboxylates (of the general form [RZn(OOCR')]) have received much less attention. In 1965, Coates reported the synthesis of methylzinc acetate, a material that was insoluble in benzene and proposed to have a polymeric structure.³³ Methylzinc acetate could be dissolved in excess pyridine, and a dimeric $[MeZn(\mu-OOCCH_3)(py)]_2$ species was proposed, although the molecular weight, determined by cryoscopy, decreased with increasing dilution. Since then, although the reactivity of ethylzinc carboxylates has been reported,³⁴ very few structural studies have been conducted. Crystal structures are known for a small number of aryl carboxylate derivatives:³⁵ ethylzinc 2,6-bis-(2,4,6trimethylphenyl)benzoate was found to form $[EtZn(\mu_2 -$ OOCR)]₂ dimers, whereas ethylzinc benzoate was found to be a cyclic hexamer of the form $[EtZn(\mu_3 - OOC(C_6H_5))]_6$. Recently, a pentanuclear structure has also been found by Redshaw et al. for complexes of the form $[Zn_5(C_6F_5)_4(Ar')_6] \cdot x(toluene)$, where Ar' = 2-chlorobenzoate or 2,4,6-trimethylbenzoate and x = 1.5 and 2, respectively.⁴⁰ Of the aliphatic carboxylate derivatives, several complexes have been prepared for which the carboxylate group contains a second coordinating functionality,

[RZn(OOCR'X)] (X = OH, NH₂, SH);^{27,36-38} a variety of structures have been observed, including tetrameric rings of $[RZn(\mu_2 \text{-}OOCR'(\mu_2 \text{-}X))] \text{ units } (R = Et; R'X = CPh_2(NH_2)),$ more complex structures such as $[Zn_6R_3(\mu_3-OOCR'(\mu_2-X))_3L_3]$ $(R = Et; R'X = CPh_2(OH); L = solvent)$ ³⁶ and extended polymers such as $[RZn(\mu_2 - OOCR'(\mu_2 - X))(py)]_n$ (R = Et; R'X $= (CH_2)_2 SH).^{27}$

Previously, we reported³⁹ that the reaction between $ZnEt_2$ and $Zn(OAc)_2$ in toluene gave an unusual pentameric complex with a ligand stoichiometry of OAc:Et of 3:2 ($[Zn_5(\mu_3 - OAc)_6(Et)_4], 1;$ Figure 1). This structure is favored in the solid state and in solution (benzene, toluene), regardless of the reagent excess and synthetic route (ligand exchange between $ZnEt_2$ and $Zn(OAc)_2$ or reaction between ZnEt₂ and acetic acid). As mentioned above, the same core pentanuclear structure was subsequently also reported by Redshaw et al. for various aryl zinc aryl carboxylates.40

One area in which zinc carboxylate reagents have shown significant promise is as catalysts in the alternating copolymerization of epoxides and carbon dioxide (Scheme 1). The copolymerization of propylene oxide (PO) and CO₂ was first reported by Inoue et al. in 1969, using ZnEt₂/water as the catalyst mixture;¹³ since this early discovery, many advances in activity, selectivity, and polymer quality have been made, and several detailed and comprehensive reviews have been published.^{15,41-44} Zinc carboxylate motifs are common among catalysts for this copolymerization: many early zinc catalysts were based on mixtures of ZnEt₂ and di- and trihydric ligands, including dicarboxylic and hydroxycarboxylic acids.¹⁴ Indeed, the most widely applied heterogeneous catalyst for the copolymerization of PO and CO₂ is zinc glutarate $[Zn(O_2C(CH_2)_3CO_2)]_n$.^{15,45} Despite its broad utility, understanding and improving surface active site structure(s) of zinc glutarate have remained extremely challenging. Indeed, syntheses of this material are sensitive to the

Received: January 4, 2011 Published: March 23, 2011



Figure 1. Pentanuclear structure of the discrete complex $[Zn_5(OAc)_6-(Et)_4]$, **1**, formed by reaction between $ZnEt_2$ and $Zn(OAc)_2$, in toluene (white bonds correspond to ethyl groups; black bonds correspond to acetate groups).





^{*a*}X = initiating group provided by the catalyst, such as halide or carboxylate; EG = polymer end-group, usually H; R, R' = H, alkyl, aryl group.

nature of the zinc precursor, stirring method, temperature, and additives. Recently, Eberhardt et al. prepared zinc glutarate derivatives from diethyl zinc, glutaric acid, and SO₂, which showed excellent productivities.¹¹ In contrast to catalysts prepared using dicarboxylic acids (such as glutaric acid), those prepared from monocarboxylic acids have been much less explored. An early study by Inoue et al.¹⁴ showed only low activity of $ZnEt_2/mono$ -carboxylic acid mixtures (acetic acid, benzoic acid) toward the copolymerization of PO and CO₂ in dioxane at 35 °C and 40 atm of CO₂; however, to our knowledge, detailed studies using more forcing conditions or with other epoxides have not been carried out for these catalyst systems.

Herein, we present our findings that both the ligand stoichiometry and nuclearity of the complex formed from the reaction between $ZnEt_2$ and $Zn(OAc)_2$ depend on the nature of the solvent. In addition, we have carried out preliminary testing of the activity of the well-defined ethylzinc acetate complexes toward copolymerization of CO_2 and cyclohexene oxide (CHO).

RESULTS AND DISCUSSION

It is well known that coordinating ligands can lower the nuclearity of heteroleptic zinc species; for example, for alkylzinc carbamato ([RZn(OOCNR'₂)]) and alkylzinc alkoxide ([RZn(OR')]) species, the addition of pyridine breaks up the discrete tetrameric complexes ([RZn(μ_3 -XR')]₄) to form dimers ([RZn(μ_2 -XR')(py)]₂).^{32,37} Previously, we showed that the reaction between equimolar quantities of ZnEt₂ and Zn(OAc)₂ in toluene or benzene yielded the pentanuclear complex, **1**, and excess ZnEt₂.³⁹ On the other hand, the addition of one equivalent



Figure 2. Selected regions of the ¹H NMR spectrum (C_6D_6) of [EtZn(OAc)(py)], **2** (see Figure S3, Supporting Information, for the complete spectrum).

of pyridine per Zn to an equimolar mixture of $ZnEt_2$ and $Zn(OAc)_2$ enabled isolation of compound 2 [EtZn(OAc)(py)] in 72% yield. The ¹H NMR spectrum of 2 showed ligand ratios of OAc:Et:py of 1:1:1 (Figure 2). As shown in Table 1, the ¹H NMR chemical shifts of the ethyl and acetate resonances are shifted much further downfield compared to 1. Both the ¹H and ¹³C-{¹H} NMR spectra show that the py resonances are shifted relative to free py in d_6 -benzene, demonstrating that the py is strongly bound to the complex in solution.

Crystals of **2** were obtained directly from the saturated reaction mixture (toluene), and X-ray diffraction experiments confirmed the 1:1 ligand ratio, showing **2** to be constructed of EtZn(OAc)(py) monomeric units (Figure 3) that link together to form an extended chain (Figure S1, Supporting Information).

In contrast to 1, the acetate groups of 2 are bound in a μ_2 coordination mode, with pyridine occupying the fourth coordination site of each tetrahedrally coordinated zinc. The Zn–O bond lengths of 2 (2.014(3) and 2.046(2) Å) are comparable to the Zn–O bond lengths of 1 (1.997(2)–2.1695(17) Å), and the Zn–N bond length (2.111(3) Å) is comparable to Zn–N bond lengths in related carbamato species (2.0786(17) Å)³⁶ and to Znbound py species (2.0339(8) Å).⁴⁶

Pulsed gradient spin—echo (PGSE) NMR spectroscopy allows determination of molecular diffusion coefficients, from which hydrodynamic radii can be estimated.⁴⁷ The diffusion coefficient of **2** in C_6D_6 was estimated to be 1.0×10^{-9} m² s⁻¹, which corresponds to a hydrodynamic radius of 3.5 Å; this value matches that estimated from the crystal data for the monomeric [EtZn(OAc)(py)] unit, based on four monomers per unit cell and a unit cell occupancy of 68%. On the basis of the measured and calculated values, it is likely that **2** exists as a monomer in solution.

The coordination of the py groups in the solid state is also supported by IR data; the absorption bands associated with the vibrations of the pyridine ring are shifted to higher frequency (free pyridine vibrations at 1581, 1030, and 604 cm⁻¹; adduct vibrations at 1605, 1041, and 614 cm⁻¹, respectively).⁴⁸ The difference, Δ , between the asymmetric and symmetric carboxylate stretches is 113 cm⁻¹, within the range for bridging acetate groups,⁴⁹ but slightly lower than that of 1 (165 cm⁻¹), which may be an indication of the difference in the acetate bridging mode (μ_2 for 2 compared to μ_3 for 1).

	1	H NMR chemical shif	t (ppm)	¹³ C{ ¹ H} NMR chemical shift (ppm)				
group	1	3	free py ⁵⁰	1	3	free py ⁵⁰		
-OOCH ₃	1.89	2.07		181.2	179.7			
$-CH_2CH_3$	1.56	1.71		12.9	14.0			
py ortho		8.60	8.53		149.5	150.3		
py para		6.81	6.98		138.5	135.3		
py meta		6.55	6.66		124.9	123.6		

Table 1. Comparison of the Chemical Shifts (in C_6D_6) of [EtZn(OAc)(py)], 2, with [$Zn_5(OAc)_6(Et)_4$], 1, and Free Pyridine (py)



Figure 3. Structure of the asymmetric unit of [EtZn(OAc)(py)], 2.



Figure 4. ¹H NMR spectrum (THF- d_8) of 3. Peak marked with "*" is residual solvent; peak marked with " Δ " is due to small amounts of (dissolved) ethane.

The analogous reaction, adding one equivalent of tetrahydrofuran (THF) to a toluene solution of $ZnEt_2$ and $Zn(OAc)_2$, yielded an opaque suspension that could not be fully characterized; however, the reaction between equimolar quantities of $Zn(OAc)_2$ and $ZnEt_2$ directly in THF yielded a product, **3**, with the molecular formula EtZnOAc (¹H NMR spectroscopy, Figure 4). The use of an excess of $Zn(OAc)_2$ (3:2 OAc:Et, as found for 1) yielded the same product, **3**, contaminated with excess $Zn(OAc)_2$ (NMR, IR; not shown). Crystals of **3** were obtained by slow evaporation from a THF solution, and X-ray



Figure 5. Molecular structure of the asymmetric unit of **3**, demonstrating the tetrahedrally coordinated zinc atoms and the acetate bridging arrangement that leads to the extended sheet structure (Figure S2, Supporting Information).

diffraction showed that the structure consists of dimeric $[EtZn(OOCCH_3)]_2$ units (Figure 5). The asymmetric units are connected to one another via bridging of neighboring μ_3 -acetate groups to form two-dimensional sheets of 16-membered $[Zn(OAc)]_4$ rings joined by Zn_2O_2 nodes (herringbone structure; Figure S2, Supporting Information). Interestingly, no molecules of THF remained bound in the solid state, despite the great excess present during crystallization. The Zn–O bond lengths in the structure are comparable to those for 1 and 2, lying within the range 1.977(7)-2.137(7) Å. The O–Zn–O bond angles of the dimeric repeat unit are $75.1(3)^\circ$ and $77.0(3)^\circ$, which are comparable to the O–Zn–O angles of the fourmembered rings of 1; the remaining O–Zn–O angles range between $92.5(3)^\circ$ and $107.9(3)^\circ$.

The 1:1 ligand ratio and absence of bound THF are supported by elemental analysis (calculated C 31.30, H 5.25, found C 31.27, H 5.14) and ¹H NMR spectroscopy (Figure 4): when redissolved in d_8 -THF, the only THF signals observed were due to residual solvent; when dissolved in d_6 -benzene (vide infra), no THF signals were observed.

The PGSE NMR spectrum of 3 in d_8 -THF gave an estimate of the diffusion coefficient of 1.7×10^{-9} m² s⁻¹, which corresponds to a hydrodynamic radius of 2.7 Å. The radius of the dimeric unit estimated from the crystal data was 3.7 Å, based on four dimers

per unit cell and a unit cell occupancy of 75.2%. The values are comparable, indicating that the sheet structure is likely to be disrupted and that 2 exists as a discrete dimer when solvated by excess THF. It seems likely that the acetate groups would favor a μ_2 -bridging coordination in an isolated (solvated) dimer, as solvent molecules could occupy the fourth coordination site of the zinc atoms; however, no evidence for such a change in coordination has been obtained.

To investigate the solvent dependence and lability of the structures of the complexes, isolated 1 and 3 were dissolved in d_8 -THF and d_6 -benzene, respectively, and their structures studied by ¹H NMR spectroscopy. Isolated 3 was largely insoluble in benzene- d_6 at room temperature but, when heated, yielded a clear solution, which remained on cooling to 25 °C. The ¹H NMR spectrum of the cooled solution showed resonances of the 3:2 pentanuclear complex (1) and those of free ZnEt₂; the sum of the integration of the ethyl peaks gave a ratio of [OAc]:[total Et] of 1:1, as expected. Similarly, attempted dissolution of isolated 1 in THF- d_8 at room temperature yielded a suspension with a large amount of undissolved solid, but, on heating the mixture to reflux (70 $^{\circ}$ C), the solid dissolved to give a clear solution, which remained on cooling to 25 °C. The ¹H NMR spectrum of the cooled solution showed total ligand ratios of 3:2 [OAc]:[Et], but the acetate resonance was shifted downfield with respect to that of 3, toward that of free $Zn(OAc)_2$. PGSE of the clear solution at room temperature gave an estimate of the hydrodynamic radius of the species in solution of 2.5 Å, comparable to 3; the expected radius of 1 was 5.1 Å, based on the crystal structure data.³⁹ From the ¹H NMR spectrum, it is believed that the solution contained the dimeric, 1:1 species (3) and excess $Zn(OAc)_2$ in dynamic exchange, rather than the pentanuclear complex. Addition of one equivalent of $ZnEt_2$ per mole of $[Zn_5(OAc)_6(Et)_4]$ to the solution gave a ¹H NMR spectrum equivalent to that of 3.

It can be concluded that the pentanuclear complex, 1, is strongly favored in aromatic solvents and that ethylzinc carboxylates dissolved in aromatic solvents will revert to the pentanuclear complex regardless of their ligand stoichiometry prior to dissolution. The process of interchanging between the 1:1 dimer and the 3:2 pentanuclear structure is accelerated by heating, presumably acting to disrupt the extended sheet and discrete complex structures, respectively.

In line with the results for derivatives containing carboxylates with a second coordinating functionality,^{27,36–38} the two polar, donating solvents impose a preference for a 1:1 ligand ratio in the ethylzinc carboxylate complexes; however, whereas py acts as an additional, permanent ligand, THF acts as a labile ligand that does not remain bound in the solid state; as such, the pyridine adduct forms as monomers of [EtZn(OAc)(py)], whereas the product formed in THF exists as $[EtZn(OAc)]_2$ dimers. The difference between the behavior of pyridine and THF can be explained by the higher donor number of py compared to THF but also by the higher polarity of py (greater driving force to bind to the metal center) and the greater acceptor ability:⁵¹ the enhanced electrophilic nature of py compared to THF is likely to introduce a significant back-donation (π -accepting character) to the Zn-py bond.

The formation of a discrete complex with unequal numbers of ligands (3:2 OAc:Et for the acetate derivative) in toluene and benzene solutions is explained by the need to minimize the polarity of the complex with respect to its outer coordination shell: in 1, the ethyl and acetate methyl groups are directed outward toward the solvent, keeping the polar Zn-O bonds

more protected toward the center of the structure. It is not clear, however, whether the observed structure "appears" less polar than a hypothetical 1:1 cubane structure similar to that seen for the ethylzinc alkoxides. It is possible that the pentanuclear arrangement is structurally more compact than other, higher structures or any attainable structures with 1:1 ligand ratios.

The tendency for the complexes to revert to the ligand ratio and structure dictated by the preference of the solvent (regardless of the structure that the solid possesses prior to dissolution) indicates the lability of the complexes and, importantly, the great influence the solvent parameters exert on the structures of organometallic complexes.

CO₂/CHO Copolymerizations. The results of CO₂/CHO copolymerization studies using 1 and 3 are summarized in Table 2. Preliminary experiments demonstrated no activity for either complex toward PO copolymerization at 15 atm CO₂; however, both were active toward cyclohexene oxide (CHO) at this pressure (in neat epoxide). It is worth noting that copolymerizations using zinc glutarate and other zinc carboxylate-based catalysts are frequently carried out at much higher pressures of CO₂ (40 atm and above).

The donating abilities of epoxides toward zinc complexes have been reported to be lower than that of THF;⁵² however, it is plausible that the same preference for the 1:1 ligand ratio occurs for CHO as for THF. It may be expected, therefore, that 1 would segregate into the 1:1 complex (3) and excess $Zn(OAc)_2$; as such, 1, 3, and $Zn(OAc)_2$ alone were tested in the copolymerization reactions to compare activity. Complex 2 showed only trace quantities of polymer formation; it is proposed that the strongly bound pyridine coligand could hinder epoxide coordination and thus retard copolymerization.

In the absence of CO₂ (1 atm N₂), both 1 and 3 were active catalysts for the homopolymerization of neat CHO, yielding a highly viscous liquid (polycyclohexene oxide) after 10 h (Table 2, rows 1 and 2). The yields of the isolated poly(cyclohexene oxide) were similar for both catalysts, and although the conversion was low (7% and 5% for 1 and 3, respectively), the M_n values were high. The low conversion and high molecular weight are comparable to the results found for epoxide homopolymerization catalyzed by alkylzinc alkoxides,⁴³ indicating that only a small proportion of the metal sites were active for catalysis. The low PDIs of the polymers ($M_w/M_n = 1.6$ and 1.5 for 1 and 3, respectively) demonstrate that, for the active zinc sites, the rate of propagation is somewhat higher than the rate of initiation.

At 15 atm CO₂ and in neat CHO, both 1 and 3 were moderately active catalysts for the copolymerization. The TOFs decreased with increasing reaction time (3 to 7.5 h), which corresponded to a decrease in reaction rate due to an increase in the viscosity of the reaction mixture. The conversion was marginally higher for 3 than 1 at the 3 h time point (Table 2; rows 4 and 6), and 1 had a much higher proportion of ether linkages after 3 h than 3. By 7.5 h, the discrepancy had disappeared and both catalysts had approximately the same conversion and the same proportion of ether linkages. The molecular weight of the copolymer catalyzed by 1 was considerably higher after 3 h than both the equivalent copolymer catalyzed by 3 and the polymer catalyzed by 1 after 7.5 h ($M_{\rm n}$ 44 800, 12 900, and 12 900 g mol⁻¹, respectively). The reduction in $M_{\rm p}$ with time for 1 is thought to be caused by initial homopolymerization to generate high molecular weight poly-(cyclohexene oxide) chains (which represent a higher proportion of the total chains) followed by copolymerization and chain

catalyst	$T/^{\circ}C$	$p(CO_2)/atm$	time/h	% conversion ^{<i>a</i>}	% carbonate ^b	% cyclic carbonate ^c	$M_{\rm n}{}^d imes 10^3/{ m gmol}^-$	¹ PDI ^d	TOF ^e	$\mathrm{TON}^{\mathrm{f}}$	
1	25	0	10	7		0	464	1.6	2	35	
3	25	0	10	5		0	234	1.5	1	16	
$[(cC_5H_9)_7Si_7O_11(OSiMePh_2)]_2Zn_4Me_4$	120	0	24	13		0			1	36	
ref 12											
1	80	15	3	24	39	3	44.8	2.5	24	128	
1	80	15	7.5	39	66	4	12.9	10.2	16	232	
3	80	15	3	32	66	2	10.8	10.2	31	184	
3	80	15	7.5	41	66	2	12.9	9.9	16	240	
$Zn(OAc)_2$	80	15	7.5	31	67	2	5.33	14.2	13	185	
$[(cC_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2Zn_4Me_4$	80	80	24	34	92	2	10.6	10.8	3	95	
ref 12											
SiO ₂ -tethered ZnEt ₂	120	80	24	6	93		9.00	5.3	1		
ref 12											
$Al(O^iPr)_3$	90	20	18	51	9.1		15.0	2.0	9	579	
ref 53											

^{*a*} Conversion was calculated as mol polymer/mol initial CHO. ^{*b*} Determined by comparison of the integration of the resonances at δ = 3.45 (ether linkage) and 4.65 ppm (carbonate linkage) in the ¹H NMR spectrum (CDCl₃). ^{*c*} Determined by comparison of the integrals of the resonances at δ = 3.45 (polycarbonate) and 4–4.1 (cyclic carbonate) ppm in the ¹H NMR spectrum (CDCl₃). ^{*d*} Determined by gel-permeation chromatography in THF, using narrow M_w poly(styrene) standards. ^{*e*} Calculated as mol polymer/mol Zn per h. ^{*f*} Productivity, calculated as grams of polymer per gram of Zn used.

transfer reactions to give shorter chains. The MALDI-ToF spectra of the copolymers catalyzed by 1 and 3 showed that, for both catalysts, the only observable polymer end-groups were hydroxyl groups, which is indicative of a chain transfer mechanism (Figures S4 and S5, Supporting Information). In line with the ¹H NMR spectroscopy results, the MALDI-ToF spectrum of the polymer catalyzed by 1 showed much higher quantities of ether linkages after 3 h compared to the equivalent copolymer catalyzed by 3.

Despite the reported¹⁴ lack of activity toward PO, $Zn(OAc)_2$ alone was surprisingly active under the current reaction conditions and yielded a copolymer with an equivalent proportion of ether and carbonate linkages after 7.5 h to that produced by 1 and 3. In general, however, both 1 and 3 showed a higher activity and higher performance in terms of productivity (per gram Zn); in comparison to the $Zn(OAc)_2$, the M_n values of the copolymers formed by 1 and 3 were higher and the PDIs narrower, demonstrating the improved behavior of these catalysts. In light of the expected segregation of 1 to 3 plus $Zn(OAc)_2$, the slightly lower activity of 1 compared to pure 3 after 3 h is explained by the lower activity of $Zn(OAc)_2$; the difference in reactivities means that the rates become comparable only after 7.5 h (16 Zn⁻¹ h⁻¹).

The results for 1 and 3 are comparable to recently reported anchored alkylzinc species (Table 2, rows 10 and 11) and the related metal alkoxide $Al({}^{i}OPr)_{3}$ (Table 2, row 12) and are likely to be similar to the zinc bis(phenoxides) reported by Darensbourg (although those systems require ~80 bar CO₂ pressures).^{12,52,53} However, although the weight-average molecular weights (M_w) of the polymers catalyzed by 1 and 3 are high and the catalyst activities are moderate, the overall quality of the polymers is low. The catalytic performance of 1 and 3 may be improved by rigorous optimization; for example, it is expected that CO₂ pressures of 40 atm and above would improve the carboxylate content of the copolymers.⁵²

In summary, we have shown that the structure of "ethylzinc acetate" in solution and the solid state is strongly affected by the nature of the solvent and that the observed structures with ligand stoichiometries of 1:1 and 3:2 are interchangeable by heating in the appropriate solvent. Copolymerization studies show promising activity toward the formation of poly(cyclohexene carbonate), but the conditions require optimization; if the polymer quality can be improved, the well-defined complex **3** could represent a low-cost, low-toxicity alternative to other, small-molecule, homogeneous catalysts.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all reactions were conducted under a nitrogen atmosphere either using standard Schlenk techniques or in a nitrogen-filled glovebox. Solvents were distilled from sodium and stored under nitrogen. Unless otherwise stated, solvents were degassed prior to use by performing three freeze-pump-thaw cycles. Deuterated solvents were dried by placing over calcium hydride, performing three freeze-thaw cycles under vacuum, refluxing for at least 48 h, distilling under vacuum, and storing under nitrogen. Diethylzinc was purchased from Aldrich, vacuum distilled, and stored in an ampule, under nitrogen, at -38 °C. Infrared (IR) spectroscopy was carried out using a Perkin-Elmer Spectrum 100 Fourier transform IR spectrometer, using dried Nujol (sodium). Elemental analysis was carried out using a Carlo Erba CE1108 elemental analyzer, and samples were manipulated under inert atmosphere (helium glovebag); analysis was performed by Mr. S. Boyer at London Metropolitan University, North Campus, Holloway Road, London, N7.

In general, NMR spectra were collected on a Bruker AV-400 instrument. The ¹H PGSE (DOSY) experiments were performed on a Bruker AV-500 spectrometer, equipped with a z-gradient bbo/5 mm tunable probe and a BSMS GAB 10 A gradient amplifier providing a maximum gradient output of 5.35 G/cmA. All experiments were measured using the stebpgp1s pulse program (TopSpin 2.1.3 software) at a constant temperature of 300 K and a gas flow of 400 L per hour. The spectra were collected at a frequency of 500.13 MHz with a spectral width of 4000 Hz (centered on 4 ppm) and 32768 data points. A relaxation delay of 10 s was employed along with a diffusion time (Δ) of 70 ms. Bipolar gradient pulses ($\delta/2$) of 2.2 ms and homospoil gradient pulses of 1.1 ms were used. The gradient strength of the homospoil pulse

was -17.13%. A total of 32 experiments were collected with the bipolar gradient strength, initially at 2% (first experiment), linearly increased to 95% (32nd experiment). All gradient pulses were sine shaped, and after each application a recovery delay of 200 μ s was used. The spectra were processed using an exponential function with a line broadening of 2 Hz. Further processing was achieved using the Bruker dosy software or DOSYm software (NMRtec).

Synthesis of 1, [Zn₅(OAc)₆(Et)₄]. This is described elsewhere.³⁹ Synthesis of 2, [EtZn(OOCCH₃)((C₅H₅)N)]. Diethylzinc (1.0 M in toluene, 1.90 mL, 1.90 mmol) was added to a suspension of anhydrous zinc bis(acetate) (0.35 g, 1.89 mmol) in toluene (3 mL). Pyridine (0.32 mL, 3.97 mmol) was added, forming a yellow solution. The mixture was stirred for 2 h, giving a clear, colorless solution with no particulates. Volatiles were removed in vacuo to yield a sticky, white solid. The solid was washed with hexane (5 mL) to yield a dry, white powder (0.32 g, 72%): ¹H NMR (C_6D_6) δ 8.60 (m, 2 H, pyridine *ortho*), 6.81 (tt, 1 H, $J_1 = 1.6$ Hz, $J_2 = 7.7$ Hz, pyridine para), 6.55 (m, 2 H, pyridine meta), 2.07 (s, 3 H, -OOCCH₃), 1.71 (t, 3 H, J = 8.0 Hz, $-CH_2CH_3$), 0.81 (q, 2 H, J = 8.0 Hz, $-CH_2CH_3$) ppm; ¹³C{¹H} NMR $(C_6D_6) \delta$ 179.7 (-C=O), 149.5 (pyridine ortho), 138.5 (pyridine para), 124.9 (pyridine meta), 24.3 (-OOCCH₃), 14.0 (-CH₂CH₃), $-0.8 (-CH_2CH_3)$ ppm; IR (Nujol mull) 1605 (sharp, py ν (C=C)),² 1551 (v(C=O)_{asymm}), 1438 (v(C=O)_{symm}), 1259, 1217 (sharp), 1156, 1071, 1040, 1013, 974, 941, 910, 796, 761, 703, 681, 635, 614, 590 cm $^{-1}\!\!.$ Anal. Calcd for C_9H_{13}O_2NZn: C 46.47, H 5.63, N 6.02. Found: C 46.38, H 5.62, N 5.84.

Synthesis of 3, [EtZn(OOCCH₃)]. Diethylzinc (0.40 g, 3.24 mmol) was added to a suspension of zinc bis(acetate) (0.593 g, 3.23 mmol) in tetrahydrofuran (5 mL). The mixture was stirred for 4 h to yield a clear, colorless solution. Volatiles were removed in vacuo to yield a fine, white powder (0.84 g, 5.47 mmol, 85%): ¹H NMR (THF-*d*₈) δ 1.97 (s, 3 H, $-\text{OOCCH}_3$), 1.13 (t, 3 H, J = 8.0 Hz, $-\text{CH}_2\text{CH}_3$) ppm; ¹³C{¹H} NMR (THF-*d*₈) δ 180.2 (-C=O), 23.7 ($-\text{OOCCH}_3$), 13.3 ($-\text{CH}_2\text{CH}_3$), 1.7 ($-\text{CH}_2\text{CH}_3$) ppm; IR (Nujol mull) 1584 (br) (ν (C=O)_{asymm.}), 1559 (w), 1421 (ν (C=O)_{symm}), 1362, 1319, 1232, 1177, 1165, 1039, 1022, 995, 957, 928, 900(w), 857(w), 723, 696, 623, 524 cm⁻¹. Anal. Calcd for C₄H₇O₂Zn: C 31.30, H 5.25. Found: C 31.27, H 5.14.

Copolymerization Reactions. In a typical experiment, a Schlenk tube was charged with the ethylzinc carboxylate catalyst (0.66 mmol Zn) and cyclohexene oxide (20 mL, 198 mmol) and stirred for 15 min. The solution was transferred to an oven-dried Parr reaction vessel under nitrogen, degassed, and placed under CO_2 atmosphere. The reactor was brought to 80 °C under 3 atm of CO_2 , before increasing the pressure to 15 bar and stirring for 7.5 h. The resulting polymer mixture was removed from the reactor using dichloromethane, and the solvent removed under reduced pressure. The polymeric product was obtained as a clear solid. The crude material was analyzed by ¹H NMR spectroscopy (to determine the % conversion and the % ether linkages) and by GPC (to determine the M_{nr} M_{wr} and PDI).

X-ray Crystallography. *Crystal data for* **2**: C₉H₁₃NO₂Zn, *M* = 232.57, monoclinic, *P*2₁/*c* (no. 14), *a* = 7.6301(3) Å, *b* = 16.0551(6) Å, *c* = 9.2431(3) Å, β = 109.296(4)°, *V* = 1068.69(7) Å³, *Z* = 4, *D_c* = 1.445 g cm⁻³, μ (Cu K α) = 2.953 mm⁻¹, *T* = 273 K, colorless blocks, Oxford Diffraction Xcalibur PX Ultra diffractometer; 2080 independent measured reflections (*R*_{int} = 0.0287), *F*² refinement, *R*₁(obs) = 0.0399, *wR*₂(all) = 0.1251, 1728 independent observed absorption-corrected reflections [|*F*_o| > 4 σ (|*F*_o|), 2 θ _{max} = 145°], 119 parameters. CCDC 799383.

Crystal data for **3**: $C_8H_{16}O_4Zn_2$, M = 306.95, orthorhombic, $Pca2_1$ (no. 29), a = 13.4868(5) Å, b = 9.2244(4) Å, c = 9.2241(3) Å, V = 1147.55(8) Å³, Z = 4, $D_c = 1.777$ gcm⁻³, μ (Cu K α) = 5.063 mm⁻¹, T = 173 K, colorless plates, Oxford Diffraction Xcalibur PX Ultra diffractometer; 1596 independent measured reflections ($R_{int} = 0.0448$), F^2 refinement, $R_1(\text{obs}) = 0.0396$, $wR_2(\text{all}) = 0.1342$, 1232 independent observed absorption-corrected reflections $[|F_o| > 4\sigma(|F_o|)$, $2\theta_{\text{max}} = 145^\circ]$, 130 parameters. The absolute structure of **3** was determined by a combination of *R*-factor tests $[R_1^+ = 0.0396, R_1^- = 0.0409]$ and by use of the Flack parameter $[x^+ = +0.03(15), x^- = +0.97(15)]$. CCDC 799384.

ASSOCIATED CONTENT

Supporting Information. Further experimental and X-ray crystallographic data are available in pdf format and as a CIF file free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: m.shaffer@imperial.ac.uk, c.k.williams@imperial.ac.uk.

ACKNOWLEDGMENT

This work was funded by the Engineering and Physical Sciences Research Council (EP/C544846/1 and EP/C544838/1). We thank Mr. P. Haycock and Mr. R. N. Sheppard for the PGSE experiments and helpful discussions.

REFERENCES

(1) Seyferth, D. Organometallics 2001, 20, 2940.

(2) Frankland, E. J. Chem. Soc. 1850, 2, 263.

(3) Knochel, P.; Almena Perea, J. J.; Jones, P. Tetrahedron 1998, 54, 8275.

(4) Boudier, A.; Bromm, L. O.; Lotz, M.; Knochel, P. Angew. Chem., Int. Ed. 2000, 39, 4414.

(5) Negishi, E.-i.; Matsushita, H.; Okukado, N. Tetrahedron Lett. 1981, 22, 2715.

(6) Matsushita, H.; Negishi, E. J. Am. Chem. Soc. 1981, 103, 2882.

(7) Son, S.; Fu, G. C. J. Am. Chem. Soc. 2008, 130, 2756.

(8) Knochel, P.; Singer, R. D. Chem. Rev. 1993, 93, 2117.

(9) Melzig, L.; Metzger, A.; Knochel, P. J. Org. Chem. 2010, 75, 2131.

(10) Schade, M. A.; Metzger, A.; Hug, S.; Knochel, P. Chem. Commun. 2008, 3046.

(11) Eberhardt, R.; Allmendinger, M.; Zintl, M.; Troll, C.; Luinstra, G. A.; Reiger, B. *Macromol. Chem. Phys.* **2004**, *205*, 42.

(12) Duchateau, R.; van Meerendonk, W. J.; Huijser, S.; Staal, B. B. P.; van Schildt, M. A.; Gerritsen, G.; Meetsma, A.; Koning, C. E.;

Kemmere, M. F.; Keurentjes, J. T. F. Organometallics 2007, 26, 4204. (13) Inoue, S.; Koinuma, H.; Tsuruta, T. J. Polym. Sci. Part C: Polym.

(14) Kobayashi, M.; Inoue, S.; Tsuruta, T. J. Polym. Sci. Polym. Chem. Ed. 1973, 11, 2383.

(15) Luinstra, G. Polym. Rev. 2008, 48, 192.

(16) Sarazin, Y.; Schormann, M.; Bochmann, M. Organometallics 2004, 23, 3296.

(17) Driess, M.; Merz, K.; Rell, S. Eur. J. Inorg. Chem. 2000, 2517.

(18) Kim, C. G.; Sung, K.; Chung, T.; Jung, D. J.; Kim, Y. Chem. Commun. 2003, 2068.

(19) Hambrock, J.; Rabe, S.; Merz, K.; Birkner, A.; Wohlfart, A.; Fischer, R. A.; Driess, M. J. Mater. Chem. **2003**, *13*, 1731.

(20) Kahn, M.; Monge, M.; Snoeck, E.; Maisonnat, A.; Chaudret, B. Small 2005, 1, 221.

(21) Kahn, M. L.; Cardinal, T.; Bosquet, B.; Monge, M.; Jubera, V.; Chaudret, B. *ChemPhysChem.* **2006**, *7*, 2392.

(22) Kahn, M. L.; Monge, M.; Colliere, V.; Senocq, F.; Maisonnat, A.; Chaudret, B. *Adv. Funct. Mater.* **2005**, *15*, 458.

(23) Monge, M.; Kahn, M. L.; Maisonnat, A.; Chaudret, B. Angew. Chem., Int. Ed. 2003, 41, 5321.

(24) Rataboul, F.; Nayral, C.; Casanove, M.-J.; Maisonnat, A.; Chaudret, B. J. Organomet. Chem. **2002**, 643–644, 307.

- (25) Lizandara-Pueyo, C.; van den Berg, M. W. E.; De Toni, A.; Goes, T.; Polarz, S. J. Am. Chem. Soc. 2008, 130, 16601.
- (26) Polarz, S.; Roy, A.; Merz, M.; Halm, S.; Schröder, D.; Schneider, L.; Bacher, G.; Kruis, F. E.; Driess, M. *Small* **2005**, *1*, 540.

(27) Boyle, T. J.; Pratt, H. D. I.; Alam, T. M.; Headley, T.; Rodriguez, M. A. *Eur. J. Inorg. Chem.* **2009**, 855.

(28) Gonzalez-Campo, A.; Orchard, K. L.; Sato, N.; Shaffer, M. S. P.; Williams, C. K. *Chem. Commun.* **2009**, *27*, 4034.

(29) Beek, W. J. E.; Slooff, L. H.; Wienk, M. M.; Kroon, J. M.; Janssen, R. A. J. Adv. Funct. Mater. 2005, 15, 1703.

(30) Bruce, J. M.; Cutsforth, B. C.; Farren, D. W.; Hutchinson, F. G.; Rabagliati, F. M.; Reed, D. R. J. Chem. Soc. (B) **1966**, 1020.

(31) Allen, G.; Bruce, J. M.; Farren, D. W.; Hutchinson, F. G. J. Chem. Soc. (B) 1966, 799.

(32) Boyle, T. J.; Bunge, S. D.; Andrews, N. L.; Matzan, L. E.; Sieg, K.; Rodriguez, M. A.; Headley, T. J. Chem. Mater. **2004**, *16*, 3279.

(33) Coates, G. E.; Ridley, D. J. Chem. Soc. 1965, 1870.

(34) Inoue, S.; Kobayashi, M.; Tozuka, T. J. Organomet. Chem. 1974, 81, 17.

(35) Lewinski, J.; Bury, W.; Dutkiewicz, M.; Maurin, M.; Justyniak, I.; Lipkowski, J. Angew. Chem., Int. Ed. **2008**, 47, 573.

(36) Redshaw, C.; Elsegood, M. R. J. Angew. Chem., Int. Ed. 2007, 46, 7453.

(37) Tang, Y.; Kassel, W. S.; Zakharov, L. N.; Rheingold, A. L.; Kemp, R. A. Inorg. Chem. 2005, 44, 359.

(38) Hursthouse, M. B.; Malik, M. A.; Motevalli, M.; O'Brien, P. J. Chem. Soc., Chem. Commun. 1991, 1690.

(39) Orchard, K. L.; White, A. J. P.; Shaffer, M. S. P.; Williams, C. K. Organometallics 2009, 58, 5828.

(40) Redshaw, C.; Jana, S.; Shang, C.; Elsegood, M. R. J.; Lu, X.; Guo, Z. X. Organometallics **2010**, 29, 6129–6132.

(41) Coates, G. W.; Moore, D. R. Angew. Chem., Int. Ed. 2004, 43, 6618.

(42) Darensbourg, D. J.; Mackiewicz, R. M.; Phelps, A. L.; Billodeaux, D. R. Acc. Chem. Res. 2004, 37, 836.

(43) Kuran, W. Prog. Polym. Sci. 1998, 23, 919.

(44) Kember, M. R.; Buchard, A.; Williams, C. K. Chem. Commun. 2011, 212.

(45) Chisholm, M. H.; Navarro-Llobet, D.; Zhou, Z. Macromolecules 2002, 35, 6494.

(46) Zhu, L. Y.; Xu, D.; Wand, X. Q.; Yu, G. J. Chem. Crystallogr. 2008, 38, 609.

(47) Price, W. S. Concepts Magn. Reson. 1997, 9, 299.

(48) Perelygin, I. S.; Klimchuk, M. A. J. Appl. Spectrosc. 1974, 24, 43.

(49) Nakamoto, K. In Infrared and Raman Spectroscopy of Inorganic

and Coordination Compounds Part B: Applications on Coordination, Organometallic, and Bioinorganic Chemistry; Wiley: New York, 1997; pp 59–60.

(50) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I., *Organome tallics* **2010**, *29*, 2176–2179.

(51) Gutmann, V. Coord. Chem. Rev. 1976, 18, 225.

(52) Darensbourg, D. J.; Holtcamp, M. W.; Struck, G. E.; Zimmer, M. S.; Niezgoda, S. A.; Rainey, P.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. J. Am. Chem. Soc. **1999**, *121*, 107.

(53) Zevaco, T. A.; Janssen, A.; Sypien, J.; Dinjus, E. Green Chem. 2005, 7, 659–666.