Alternating Copolymerization of Cyclohexene Oxide and CO_2 Catalyzed by Zinc Complexes with New 3-Amino-2-cyanoimidoacrylate Ligands

Mario Kröger, Cristina Folli, Olaf Walter, Manfred Döring*

Forschungszentrum Karlsruhe, Institute for Technical Chemistry (ITC-CPV), Hermann-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
Fax: (+49)-7247-822-244, e-mail: manfred.doering@itc-cpv.fzk.de

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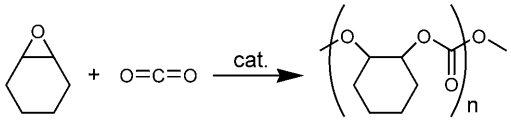
Abstract: New 3-amino-2-cyanoimidoacrylate ligands with varying steric demands have been synthesized. Zinc acetate complexes of these ligands catalyze the copolymerisation of CO_2 and cyclohexene oxide, showing high activities (TOF up to over 200 h^{-1}).

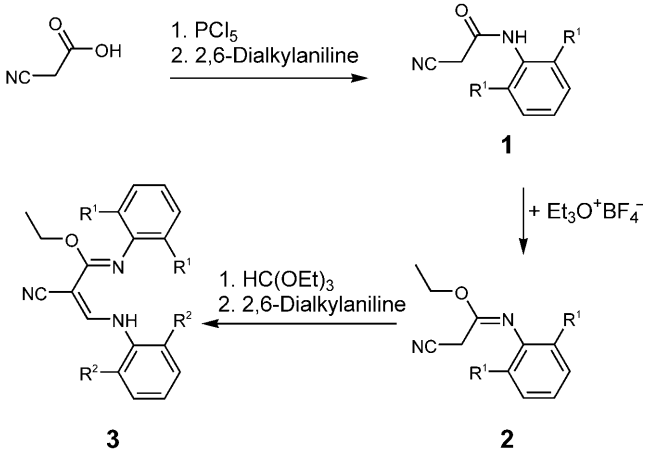
Keywords: carbon dioxide fixation; copolymerization; green chemistry; homogeneous catalysis; ligand design

The use of CO_2 as a C_1 building block is one of the most important goals in green and synthetic chemistry because it is abundance and its non-toxic, non-flammable and inexpensive properties.[1–4] The formation of aliphatic polycarbonates by catalytic copolymerization of CO_2 with epoxides (Scheme 1) is a very promising way to reach this goal.[5–7] The reaction was first discovered by Inoue and co-workers[8] and is of major interest due to the promising material properties and the biodegradability of the resulting polycarbonates. Over the past decade the field has gained new momentum by the discovery of several homogeneous, highly active catalysts like zinc phenoxides,[9] chromium porphyrins,[10] and chromium salen complexes.[11] The growing interest in copolymerization gave rise to a number of recent reviews.[12–14] Especially zinc complexes with β-diimine ligands have set new benchmarks in the homogenous catalysis of polycarbonate formation.[15] Coates et al. have shown that electron-withdrawing groups on the diimine backbone enhance catalytic activities.[16] We developed a new synthetic route towards chelating imidoester ligands with functional groups on the ligand backbone. Zinc acetate complexes thereof were made and successfully tested as catalysts for the copolymerization of cyclohexene oxide and CO_2.



Scheme 1. Copolymerisation of cyclohexene oxide and carbon dioxide.

The 3-amino-2-cyanoimidoacrylate ligands were built up gradually in four steps (Scheme 2). First, cyanoacetic acid was condensed to the corresponding acetamide **1**, preferably with *ortho*-substituted anilines, *via* chlorination of the acid.[17] Treatment of the acetamide **1** with an oxonium salt lead to the related imidoester **2**.[18] The ligand was completed by a Claisen orthoester condensation at the nucleophilic carbon of **2** to give 2-cyano-3-ethoxyimidoacrylate,[19] and subsequent substitution of the ethoxy group by an *ortho*-substituted aniline of choice yielded the desired 3-amino-2-cyanoimidoacrylates **3**.[20,21] The two final steps can be carried out in a one-pot procedure without purification of the intermediate 2-cyano-3-ethoxyimidoacrylate. By this route we have prepared five ligands with varying steric demands (**3a**–**e**). Generally, the procedure should allow for a wide range of substituents on the ligand. Thus we are able to get a broad picture of structure-activity relationships with this type of ligands.



Scheme 2. Ligand synthesis.

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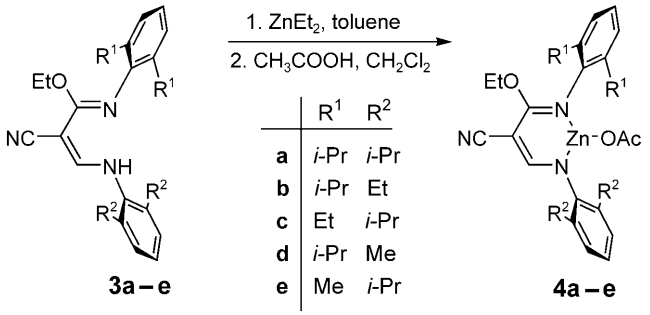

	R^1	R^2
a	*i*-Pr	*i*-Pr
b	*i*-Pr	Et
c	Et	*i*-Pr
d	*i*-Pr	Me
e	Me	*i*-Pr

Scheme 3. Complex synthesis.

Zinc acetate complexes of the ligands were made *via* the reaction with diethylzinc to produce an ethylzinc complex as intermediate. Successive treatment with acetic acid yielded the desired complexes (Scheme 2).[15,22] Acetate serves as an initiating group which mimics carbon dioxide and mechanistic studies have revealed that acetate is attacked by cyclohexene oxide in the initial step of the copolymerisation.[23] Complexes with alkoxides[15] and sulfinates[24] as initiating groups exhibit similar activities, but for reasons of consistency and comparability, acetate was chosen as initiating group throughout.

In the solid state, the zinc acetate complexes exist in the dimeric form, which is confirmed by the X-ray structures of **4a**, **c** and **e**. Figure 1 shows complex **4a** as an example. The two tetrahedral zinc centers are bridged by two acetates, the zinc-zinc distance being 4.161 Å. The bulkier sides of the ligand carrying the imidoester crystallize *anti* to each other, presumably to minimize steric repulsions.

All (3-amino-2-cyanoimidoacrylate) zinc acetates (**4**) catalyzed the copolymerization of cyclohexene oxide and CO_2. Copolymerizations were carried out in neat monomer mixtures with catalyst loadings of 0.1% at temperatures from 90–100 °C and a pressure of 4 MPa. Complexes having an ethyl or methyl group as *ortho*-substituent on one benzene ring (**4b–e**) were more active and selective than doubly isopropyl substituted **4a** (Table 1). The resulting poly(cyclohexene carbonate) had molecular weights above 15,000 g/mol and incorporated over 72% carbonate linkages. Homopolymerization of cyclohexene oxide occurred as a competing side reaction, but at 90 °C only about 10% polyether bonds were formed (Table 1). The copolymers were atactic, as ^{13}C NMR analysis revealed a random distribution of isotactic and syndiotactic carbonate. Narrow polydispersities (<1.26) denote the living character of the copolymerization.

In a recent review, catalytic activities > 200 TOF in the epoxide/CO_2 copolymerization have been defined as high (moderate: 5–200 TOF, low: < 5 TOF).[14] Thus, activities of our 3-amino-2-cyanoacrylimidic acid ester zinc acetate systems (**4e**) are high, surpassing the 200 TO h^{-1} mark. Ligands with a combination of methyl and isopropyl groups (**4d, e**) on the anilines seem to be slightly more active than the ones combining ethyl and isopropyl groups (**4b, c**). On the other hand no significant influence of the position of the larger and smaller substituents can be found. Ligands having the methyl or ethyl group on the side of the imido ester (**4c, e**) exhibit nearly the same activity than the ones having the isopropyl substituent in this positions (**4b, d**).

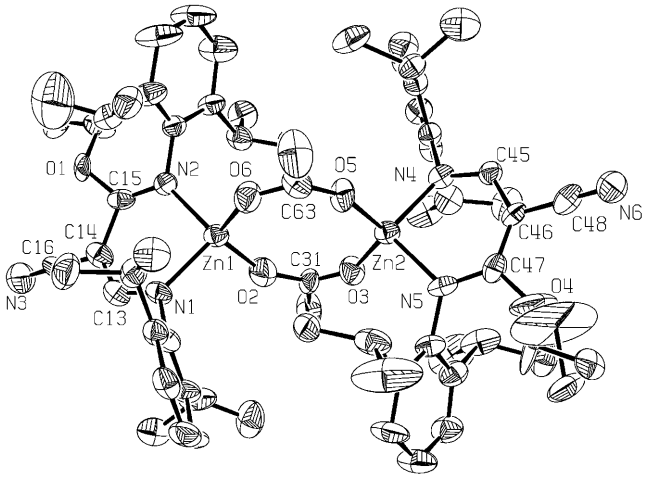

Figure 1. Structure of **6a**. Selected bond distances (Å) and angles (deg): Zn(1)–N(1) 1.989(7), Zn(1)–N(2) 1.999(7), Zn(1)–O(2) 1.937(8), Zn(1)–O(6) 1.918(7), N(1)–Zn(1)–N(2) 95.5(3), O(2)–Zn(1)–O(6) 120.1(3), O(2)–Zn(1)–N(2) 113.1(4).

Starting from these promising first results we hope to obtain even more active catalysts by systematic changes in the ligand architecture, exploiting the broad structural variety that can be synthesized based on the presented new synthetic route. In addition we will try to improve the insight into the character of the copolymerization by mechanistic studies.

Overall we have developed a flexible synthetic route towards a new class of ligands, 3-amino-2-cyanoacrylimidic acid esters, and demonstrated their ability to form zinc acetate complexes which are highly active in the copolymerization of cyclohexene oxide and CO_2.

Experimental Section

General Remarks

All reactions with air- or water-sensitive compounds were carried out under dry argon using standard Schlenk line techniques. NMR spectra were recorded on a Bruker spectrometer (250 MHz for ^1H, 62.9 MHz for ^{13}C) at 293 K. Mass spectra were obtained using electron ionization (EI), electron spray ionization (ESI) or field ionization (FI). FI and EI spectra were recorded with Micromass GCT and Finnigan MAT GCQ spectrometers, ESI spectra were recorded with a Hewlett-Packard 1100 MSD spectrometer. Melting points were ei-

Table 1. Performance of catalysts in the cyclohexene oxide/CO_2 copolymerization.

Catalyst[a]	t [h]	T [°C]	p (CO_2) [MPa]	TON[b]	TOF[b] [h^{-1}]	$g_{poly}\ g_M^{-1}$ [h^{-1}]	Carbonate linkages [%][c]	M_n[d] [kg mol^{-1}]	M_w/M_n
4a	2	100	4	170	135	293	58	12.6	1.72
4b	2	100	4	327	164	356	72	20.0	1.26
4c	2	90	4	315	158	343	86	17.5	1.16
4d	2	90	4	367	183	399	88	24.5	1.15
4e	2	100	4	396	198	430	75	15.8	1.21
4e	1	90	4	210	210	456	88	10.0	1.16

[a] A [CHO]:[Zn] ratio of 1000:1 was used throughout.
[b] Mole of CHO consumed per mole of zinc (per hour for TOF).
[c] Determined by ^{1}H NMR.
[d] Determined by GPC in THF.

ther determined by using capillaries in a melting point apparatus (Büchi), or by differential scanning calorimetry (DSC) with a Mettler Toledo DSC822e. IR spectra were recorded with a Perkin Elmer System 2000 FT-IR.

Materials

2,6-Diisopropylaniline was distilled under vacuum and cyclohexene oxide was distilled from calcium hydride under vacuum. All other reagents were purchased commercially and used as received.

General Synthetic Procedures

2-Cyano*-N-*(2,6-diisopropylphenyl)acetamide (**1a**): Cyanoacetic acid (12.76 g, 0.15 mol) was added to a stirred suspension of phosphorus pentachloride (31.27 g, 0.15 mol) in dichloromethane (450 mL) at ambient temperature. The reaction mixture was heated at reflux for 30 min. After cooling, 2,6-diisopropylaniline (17.73 g, 0.10 mol) was added in 10 min and the reaction mixture was heated for 2 h under reflux. It was then cooled in an ice/water bath, and water (200 mL) was added. After stirring for 30 min, the reaction mixture was neutralized by addition of sodium carbonate solution. The water phase was extracted twice with dichloromethane; the organic phases were then collected and dried over Na_2SO_4. The solvent was removed under reduced pressure and the obtained white solid was recrystallized from toluene and dried in vacuum; yield: 23.3 g (0.095 mol, 95%); mp 160–162 °C. ^{1}H NMR ($CDCl_3$): δ = 7.73 (s, 1H, NH), 7.28–7.07 (m, 3H, H_{aryl}), 3.33 (s, CH_2), 2.87 (m_7, 2H, CH), 1.07 (d, 12H, CH_3). EI^+-MS: *m/z* = 244 (M^+).

Ethyl 2-cyano*-N-*(2,6-diisopropylphenyl)ethanimidoate (**2a**): A mixture of 2-cyano-*N*-(2,6-diisopropylphenyl)acetamide (**1a**; 14.70 g, 60 mmol) and a 1.0 M solution of triethyloxonium tetrafluoroborate in dichloromethane (66 mL, 66 mmol) was stirred for 5 days at ambient temperature. The solvent was removed under vacuum and the residue was washed twice with absolute diethyl ether. Then the residue was taken up in 60 mL of absolute diethyl ether and cooled to 0 °C. Triethylamine (9.2 mL, 66 mmol) was slowly added, and the mixture was stirred at room temperature for 2 h. The organic phase was separated and the residue was washed three times with absolute diethyl ether. The diethyl ether solutions were collected, dried over Na_2SO_4, and the solvent was removed under reduced pressure. Distillation of the residue (13.7 g) gave the pure product; yield: 7.52 g (28 mmol, 46%); bp 103 °C. ^{1}H NMR (DMSO-d_6): δ = 7.18–6.97 (m, 3H, H_{aryl}), 4.35 (q, 2H, OCH_2), 3.40 (s, 2H, CH_2), 2.72 (m_7, 2H, CH), 1.34 (t, 3H, CH_3), 1.14 (d, 6H, CH_3), 1.06 (d, 6H, CH_3); ^{13}C NMR (DMSO-d_6): δ = 151.84, 142.00, 137.54, 124.24, 123.40, 115.21, 62.87, 27.98, 23.52, 22.78, 19.57, 14.30; EI^+-MS: *m/z* = 273 (M^+).

Ethyl 2-cyano-3-[(2,6-diisopropylphenyl)amino]*-N-*(2,6-diisopropylphenyl)prop-2-enimidoate (**3a**): A mixture of ethyl 2-cyano-*N*-(2,6-diisopropylphenyl)ethanimidoate (**2a**; 1.18 g, 4.2 mmol), triethyl orthoformate (0.61 g, 4.2 mmol), and acetic anhydride (5.47 g, 8.4 mmol) was refluxed for 5 h. The solvent was removed under reduced pressure. The resulting thick oil was dissolved in methanol (5 mL), 2,6-diisopropylaniline (0.93 g, 4.7 mmol) was added and the solution was refluxed for 30 min. The reaction mixture was then stored overnight at 5 °C and the product crystallized. Recrystallization from methanol afforded colorless crystals of the product; yield: 0.77 g (1.68 mmol, 42%); mp 157 °C. ^{1}H NMR ($CDCl_3$): δ = 7.53 (d, 1H, C=CH), 7.28–7.02 (m, 6H, H_{aryl}), 4.37 (d, 1H, NH), 3.72 (q, 2H, CH_2), 3.04 (m_7, 2H, CH), 2.89 (m_7, 2H, CH), 1.18 (t, 3H, CH_3), 1.13 (d, 6H, CH_3), 1.10 (d, 6H, CH_3); ^{13}C NMR ($CDCl_3$): δ = 156.8, 145.4, 145.0, 139.0, 135.9, 128.7, 124.4, 124.2, 123.3, 29.1, 28.8, 28.7, 24.3, 24.0, 23.9, 23.3, 22.9, 15.6; IR (KBr): ν = 3185 (N–H), 2198 (C=N), 1647 (C=N), 1587 cm^{-1} (C=C); EI^+-HR-MS: *m/z* = 459.3255, calcd. for $C_{30}H_{41}N_3O$: 459.3250; δ = 0.5 mDa.

[(3a)Zn(OAc)]$_2$ **(4a)**: Zinc acetate complexes of the ligand were prepared *via* the corresponding ethylzinc complex by literature procedures. X-ray quality crystals were obtained by covering a methylene chloride solution with pentane. ^{1}H NMR ($CDCl_3$): δ = 7.46 (d, 1H, C=CH), 7.30–6.90 (m, 6H, H_{aryl}), 4.09 (q, 2H, CH_2), 2.98 (m_7, 4H, CH), 1.86 (bs, 3H, $OC(O)CH_3$), 1.36 (t, 3H, CH_3), 1.03 (m, 12H, CH_3). MS (ESI): *m/z* = 582 ($M^+ + 1$).

General Procedure for Copolymerisation Reactions

An autoclave (Parr) was heated to 95 °C under vacuum for 16 h and cooled under vacuum. [(**4a**)Zn(OAc)] (**6a**; 48 mg, 0,082 mmol) and cyclohexene oxide (7.87 g, 82 mmol) were brought into the autoclave, which was then heated to reaction

temperature and pressurized with CO_2 to the appropriate pressure (40 bar). After 2 h the reactor was cooled, vented and a small sample taken for analysis. The resulting polycarbonate was dissolved in CH_2Cl_2 (5 mL), precipitated from MeOH (20 mL), collected and dried under vacuum to constant weight.

Crystallographic Data on [(3a)Zn(OAc)]$_2$ (4a)

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-266169. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44(1223)336–033; E-mail: deposit@ccdc.cam.ac.uk].

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