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Polymerisations of ε-caprolactone and β-butyrolactone with Zn-, Al- and Mg-based organometallic complexes

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Abstract

The reaction of $EtAlCl_2$ with 1,2-$\{LiN(PMes_2)\}_2C_6H_4$ (Mes = 2,4,6-$Me_3C_6H_2$) and of butyloctylmagnesium with 1,2-$\{NH(PPh_2)\}_2C_6H_4$ gave [AlEt(1,2-$\{N(PMes_2)\}_2C_6H_4$-κ^2N,N')(THF)] (**1**) and [Mg(1,2-$\{N(PPh_2)\}_2C_6H_4$-κ^2N,N')$(THF)_2$] (**2**), respectively. Complexes **1** and **2** were fully characterised by NMR (^1H, ^{13}C, ^{31}P) and IR spectroscopy and mass spectrometry. Complexes **1** and **2** were employed as catalysts in the polymerisation of ε-caprolactone, which produced polymers with a narrow molecular weight distribution. For comparison the polymerisations of ε-caprolactone and β-butyrolactone were carried out with the Zn complex [ZnPr{1-N$(PMes_2)$-2-N$(PHMes_2)C_6H_4$-κ^2N,N'}] (**3**) as catalyst, which produced polymers with narrow molecular weight distributions and high molecular weights.

Keywords: Magnesium bisamido complex; Aluminium bisamido complex; Molecular structures; Polymerisation of ε-caprolactone and β-butyrolactone

1. Introduction

Aliphatic polyesters are an important class of polymers due to their extensive use as commodity thermoplastics [1] and their significant biomedical applications [2]. Among the many polyesters, special interest is devoted to poly(ε-caprolactone) (PLC) and poly(3-hydroxybutyrate) (PHB). The interest in the former relates to its miscibility with different commercial polymers [styrene–acrylonitrile copolymers (SAN), acrylonitrile–butadiene–styrene copolymers (ABS), PVC, nitrocellulose] [3], its biodegradability [4], its adhesive properties at low temperatures [3c] and its ability to disperse pigments [5]. The polyester PHB occurs naturally as an isotactic, highly crystalline polymer with biodegradable and biocompatible properties [6]. This stereoregular polymer is produced in nature by microorganisms, but it has low thermostability, and melt processing is therefore difficult. However, copolymerisation with other lactones has produced polymers with improved thermal stability and better processability [7]. Ring-opening polymerisation of cyclic esters is a particularly convenient method for the synthesis of polyesters as the relief of ring strain is a driving force for the polymerisation (Scheme 1). This polymerisation method allows the production of polymers with narrow molecular weight distribution and good control over the molecular weight. This control via a living polymerisation is obtained in many catalytic systems in which initiation is fast and there is almost no termination process. If termination or cyclisation become important processes (normally at high temperatures) a large deviation from the living range can be observed [8].

The most common catalysts used for the ring-opening polymerisation of polyesters are ionic alkali metal alkoxides [9], although other main group metal and covalent transition

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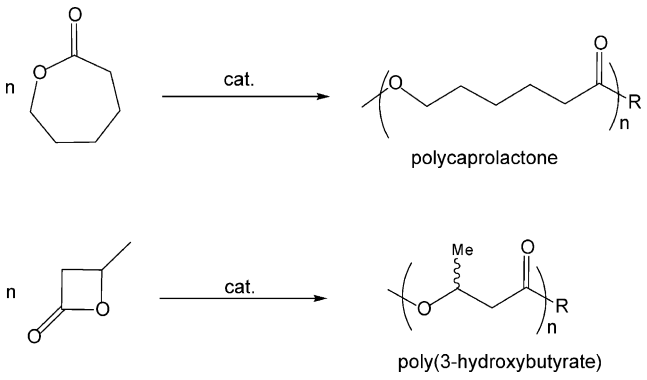


Scheme 1.

metal alkoxides have been employed [10]. Interest has been especially devoted to inexpensive and non-toxic zinc and iron alkoxides [11], although in the last few years novel Al [12], Zn [13] and Mg [14] complexes with nitrogen-based ligands were shown to exhibit remarkable activities in producing unique types of tailored and telechelic polymers. Most of the complexes are of the general formula [M(OR)L_n] in which L_n is a supporting ancillary ligand, and OR an alkoxyl group serving as an activating group.

Here we present the synthesis and characterisation of the Al complex [AlEt(1,2-{N(PMes$_2$)}$_2$C$_6$H$_4$-κ^2*N*,*N*′)(THF)] (Mes = 2,4,6-Me$_3$C$_6$H$_2$) (**1**) and the Mg complex [Mg(1,2-{N(PPh$_2$)}$_2$C$_6$H$_4$-κ^2*N*,*N*′)(THF)$_2$] (**2**). In addition, we report on the reactivity of **1** and **2** in the polymerisation of ε-caprolactone, which produced polymers with a narrow molecular weight distribution. Furthermore, for comparison we present the polymerisations of ε-caprolactone and β-butyrolactone by the Zn complex [ZnPr{1-N(PMes$_2$)-2-N(PHMes$_2$)C$_6$H$_4$-κ^2*N*,*N*′}] (**3**) [15,16] (Fig. 1), which produced polymers with narrow molecular weight distributions and high molecular weights.

2. Experimental

2.1. Materials and methods

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line, or interfaced to a high-vacuum (10^{-5} Torr) line, or in a nitrogen-filled vacuum atmospheres glove box with a medium-capacity recirculator (1–2 ppm O_2). Argon and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Hydrocarbon solvents and deuterated solvents were distilled under nitrogen from Na/K alloy. All solvents for vacuum-line manipulations were stored in vacuum over Na/K alloy in resealable bulbs. ε-Caprolactone and β-butyrolactone were distilled from CaH_2. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer scanning between 400 and 4000 cm^{-1} by using KBr disks. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on an AVANCE DRX 400 spectrometer (Bruker). The chemical shifts for the ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) at 400.13 and 100.63 MHz, respectively, with tetramethylsilane as external standard. The chemical shifts for the ^{31}P NMR spectra are reported in ppm at 161.97 MHz (with 85% H_3PO_4 external standard). The mass spectra were recorded on a VG 12-250 EI mass spectrometer (70 eV), on an FT-ICR-MS Bruker-Daltonics ESI mass spectrometer (APEX II, 7 T), and on an Ltd. ZAB-HSQ-VG for the FAB mass spectra, with 3-nitrobenzyl alcohol as matrix. The elemental analyses were recorded on a VARIO EL (Heraeus). The melting points were determined in sealed capillaries and were not corrected. $EtAlCl_2$ and butyloctylmagnesium Mg(n-C$_4$H$_9$)$_{1.5}$(n-C$_8$H$_{17}$)$_{0.5}$ were used as received from WITCO GmbH. Molecular weights of polymers were determined by the GPC method on a Waters-Alliance 2000 instrument using 1,2,4-trichlorobenzene (HPLC) as mobile phase at 150 °C. 1,2-{NH(PMes$_2$)}$_2$C$_6$H$_4$ [16], 1,2-{NH(PPh$_2$)}$_2$C$_6$H$_4$ [17] and [ZnPr{1-N(PMes$_2$)-2-N(PHMes$_2$)C$_6$H$_4$-κ^2*N*,*N*′}] (**3**) [15] were prepared according to literature procedures.

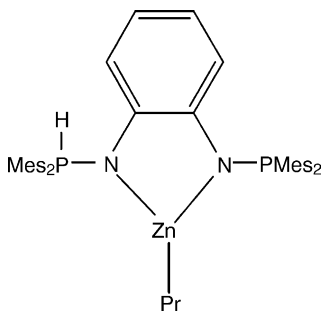


Fig. 1. Structure of [ZnPr{1-N(PMes$_2$)-2-N(PHMes$_2$)C$_6$H$_4$-κ^2*N*,*N*′}] (**3**).

2.2. Preparation of [AlEt(1,2-{N(PMes$_2$)}$_2$C$_6$H$_4$-κ^2*N*,*N*′)(THF)] (*1*)

1.6 ml of Bu^{n}Li (2.23 M in hexane) was added to a solution of 1,2-{NH(PMes$_2$)}$_2$C$_6$H$_4$ (1.15 g, 1.78 mmol) in 20 ml of toluene. The mixture was cooled to 0 °C, and a solution of $EtAlCl_2$ (0.2 ml in 10 ml of *n*-hexane, 1.78 mmol) was added dropwise. The mixture was refluxed for 30 min, filtered and concentrated. THF was added to the saturated toluene solution and the product was obtained as pale yellow air-sensitive crystals at 4 °C. Yield: 0.9 g (66%). decomp.: 224–226 °C. ^{1}H NMR (C$_4$D$_8$O, ppm): 7.05–7.19 (m, 2H in C$_6$H$_4$), 6.61 (s, 8H, *m*-H in Mes), 6.49 (m, 2H in C$_6$H$_4$), 3.6 (m, 4H, THF), 2.30 (s, 12H, *p*-CH$_3$ in Mes), 2.16 (s, 24H, *o*-CH$_3$ in Mes), 1.77 (m, 4H, THF), 1.03 (s, 3H, CH$_3$ in EtAl), −0.56 (br, 2H, CH$_2$ in EtAl). ^{31}P NMR (C$_4$D$_8$O, ppm): 27.7 (s). ^{13}C{^{1}H} NMR (C$_4$D$_8$O, ppm): 146.3 (d, $^2J_{PC}$ = 19.6 Hz, *o*-C in Mes), 138.3 (s, *p*-C in Mes), 136.6 (d, *ipso*-C in C$_6$H$_4$, $^2J_{PC}$ = 30 Hz), 130.2 (s, *m*-C in Mes), 122.3 (s, C^{4,5} in C$_6$H$_4$), 118.1 (s, C^{3,6} in C$_6$H$_4$), 114.4 (d, $^1J_{PC}$ = 38 Hz, *ipso*-C in Mes), 21.4 (s, *p*-CH$_3$ in Mes), 20.8 (d, $^3J_{PC}$ = 5.6 Hz, *o*-CH$_3$

in Mes and obscured signal of CH_3 in EtAl), 10.3 (s, CH_2 in EtAl). IR (KBr, cm^{-1}): 2920s, 1660s, 1573vs, 1474vs, 1222vs, 1122s, 1115vs, 1050s, 915vs, 832vs, 740s, 695w, 654m, 602m, 557m, 485m. MS (FAB): *m/z* (%): 701.3 [M^+-THF] (1), 685.3 [M^+-THF-CH_3] (2), 671.2 [M^+-THF-Et] (7), 644.2 [M^+-THF-Et-Al] (2), 285 $[Mes_2PN]^+$ (100), calc. for: $C_{48}H_{61}AlN_2OP_2$: M = 771.00. Found: C 73.5; H 5.08; N 3.09%; anal. calcd. for $C_{48}H_{61}AlN_2OP_2$ (771.00): C 74.78; H 7.97; N 3.63%.

2.3. Preparation of [Mg(1,2-{N(PPh$_2$)}$_2$C$_6$H$_4$-κ^{2}N,N′)(THF)$_2$] (2)

A solution of Mg(n-C_4H_9)$_{1.5}$(n-C_8H_{17})$_{0.5}$ (0.82 M in n-heptane, 2.56 ml, 2.1 mmol) in 10 ml of n-hexane was added dropwise to a solution of 1,2-{NH(PPh$_2$)}$_2$C$_6$H$_4$ (1.0 g, 2.1 mmol) in 20 ml of THF at 0 °C. The reaction mixture was stirred to room temperature for 1 h and then concentrated. The product was isolated by filtration as a yellow air-sensitive solid. Yield: 1.33 g (98%). decomp.: 153–155 °C (melts at 208–210 °C). ^{1}H NMR (C_4D_8O, ppm): 7.37-7.43 (m, 6H *o*-, *p*-H in Ph), 7.28-7.32 (m, 6H *o*-, *p*-H in Ph), 7.15-7.19 (m, 4H, *m*-H in Ph), 7.08-7.12 (m, 4H, *m*-H in Ph), 6.65-6.69 (m, 2H in C_6H_4), 6.46 (m, 1H in C_6H_4), 6.03 (m, 1H in C_6H_4), 3.61 (m, 4H in THF), 1.77 (m, 4H in THF). ^{31}P NMR (C_4D_8O, ppm): 31.6 (s). ^{13}C{^{1}H} NMR (C_4D_8O, ppm): 147.5 (d, $^1J_{PC}$ = 25.2 Hz, *ipso*-C in Ph), 142.2 (d, $^2J_{PC}$ = 14.1 Hz, *o*-C in Ph), 138.0 (d, $^2J_{PC}$ = 17.4 Hz, *ipso*-C in C_6H_4), 132.5 (d, $^1J_{PC}$ = 19.9 Hz, *ipso*-C in Ph), 131.9 (d, $^2J_{PC}$ = 20.3 Hz, *o*-C in Ph), 129.3 (s, *p*-C in Ph), 129.0 (d, $^3J_{PC}$ = 6.2 Hz, *m*-C in Ph), 128.2 (d, $^3J_{PC}$ = 5 Hz, *m*-C in Ph), 127.4 (s, *p*-C in Ph), 121.5 (s, C^4 in C_6H_4), 119.2 (d, $^3J_{PC}$ = 19.4 Hz, $C^{3,6}$ in C_6H_4), 115.4 (s, C^5 in C_6H_4), 67.7 (s, THF), 25.6 (s, THF). IR (KBr, cm^{-1}): 3052m, 2964s, 2896w, 1556s, 1470vs, 1432s, 1233vs, 1107vs, 1018s, 929vs, 869s, 817s, 746s, 700s, 611w, 508s, 471m. MS (FAB): *m/z* (%): 644.3 [M^+] (7.5), 477.3 [M^+-2THF-Mg] (15), 399.1 [M^+-2THF-Mg-Ph] (10), 291.1 $[Ph_2PNC_6H_4N]^+$ (100), calc. for: $C_{38}H_{40}MgN_2O_2P_2$: M = 642.97. Found: C 68.2; H 6.0; N 4.3%; anal. calcd. for $C_{38}H_{40}MgN_2O_2P_2$ (642.97): C 71.0; H 6.3; N 4.3%.

2.4. Polymerisation of ε-caprolactone and β-butyrolactone with [AlEt(1,2-{N(PMes$_2$)}$_2$C$_6$H$_4$-κ^{2}N,N′)(THF)] (1) as catalyst

The polymerisations were performed in a solvent-free environment. In a glove box, 5 mg of **1** (0.0065 mmol) and an equimolar amount of ε-caprolactone or β-butyrolactone were introduced into a dry reaction vessel equipped with a magnetic stirring bar. The vessel was placed in an oil bath thermostatically heated to 110 °C. The reaction was quenched with CH_2Cl_2/HCl. The polymer dissolved in CH_2Cl_2 and was precipitated with cold MeOH. The white polymer was dried to a constant weight.

2.5. Polymerisation of ε-caprolactone with [Mg(1,2-{N(PPh$_2$)}$_2$C$_6$H$_4$-κ^{2}N,N′)(THF)$_2$] (2) as catalyst

In a glove box, 5 mg of **2** (0.0078 mmol), 3 ml of toluene and an equimolar amount of ε-caprolactone were loaded into a dry reaction vessel equipped with a magnetic stirring bar. The vessel was thermostatically heated in an oil bath at 110 °C for 30 min. The reactions were quenched with CH_2Cl_2/HCl. The polymer dissolved in CH_2Cl_2 and was precipitated with cold MeOH. The white polymers were dried to a constant weight.

2.6. Polymerisation of ε-caprolactone and β-butyrolactone with [ZnPr{1-N(PMes$_2$)-2-N(PHMes$_2$)-C$_6$H$_4$-κ^{2}N,N′}] (3) as catalyst

The polymerisations were performed in a 100 ml Schlenk reactor with strong magnetic stirring under the following conditions. A stock solution was prepared by dissolving 0.047 g of **3** in 20 ml of toluene (2.35 mg/ml, 3.125×10^{-3} M). In a glove box 1 ml (3.125×10^{-3} mmol) of the stock solution was added to the reactor by using a micropipette. Then the specific amount of the cyclic lactone was added to the Schlenk reactor, which was connected to the Schlenk line and heated to either 85 ± 1 or 100 ± 1 °C for the desired amount of time. The polymerisation reaction was quenched with methanol. The polymer was obtained as a lump of transparent material. This material was dissolved in CH_2Cl_2 and the solution was poured into cold methanol and left to stand in an ice bath for several hours. The polymer which precipitated was decanted, washed with cold methanol and transferred to a Schlenk vial for drying on a vacuum line. The residual methanol solution was transferred into a flask, methanol was removed by means of a flash evaporator, and final drying was performed on a high-vacuum line to eliminate traces of monomer.

2.7. Data collection and structure determination of 1 and 2

Crystallographic data are listed in Table 1. The data were collected with a Siemens CCD (SMART) diffractometer using ω-scan rotation. Data reduction was performed with SAINT including the program SADABS for empirical absorption correction [18]. Both structures were solved by direct methods and the refinement of all non-hydrogen atoms was performed with SHELX97 [18]. H atoms were mainly calculated on idealised positions. All presentations of molecular structures in this paper were generated with ORTEP [18]. CCDC 259838 (**1**) and 259839 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 33; or deposit@ccdc.cam.uk).

Table 1
Crystal data and structure refinement for **1** and **2**

	1	**2**
Formula	$C_{48}H_{61}AlN_2OP_2$·1.5 toluene	$C_{38}H_{40}MgN_2O_2P_2$
M_r	909.11	642.97
T (K)	216(2)	208(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$C2/m$	$Pna2_1$
Z	4	4
ρ_{calc} (Mg m^{-3})	1.180	1.232
a (Å)	11.277(2)	26.248(5)
b (Å)	27.521(6)	10.106(2)
c (Å)	16.490(3)	13.072(3)
α (°)	90	90
β (°)	91.32(3)	90
γ (°)	90	90
V (Å^3)	5116.4(18)	3467.5(12)
Crystal size (mm)	0.5 × 0.5 × 0.5	0.2 × 0.1 × 0.1
Colour, habit	Pale yellow, prism	Yellow, prism
μ (mm^{-1})	0.144	0.179
F(000)	1956	1360
Radiation	Mo Kα	Mo Kα
$2\theta_{max}$ (°)	57.46	59.06
h, k, l ranges	−15 → 13; −34 → 36; −22 → 21	−33 → 34; −9 → 13; −12 → 17
Absorption correction	SADABS	SADABS
Measured reflections	16481	22325
Independent reflections	6140	7731
R_{int}	0.0350	0.0815
No. of parameters, restraints	473, 38	406, 1
R (F^2), ωR (F^2)	0.0660, 0.1245	0.1403, 0.1386
R [$F^2 > 2\sigma(F^2)$], ωR [$F^2 > 2\sigma(F^2)$]	0.0454, 0.1114	0.0597, 0.1153
Goodness-of-fit	1.056	0.934
$(\Delta/\rho)_{max}$ (e Å^{-3})	0.35	0.33
$(\Delta/\rho)_{min}$ (e Å^{-3})	−0.30	−0.28

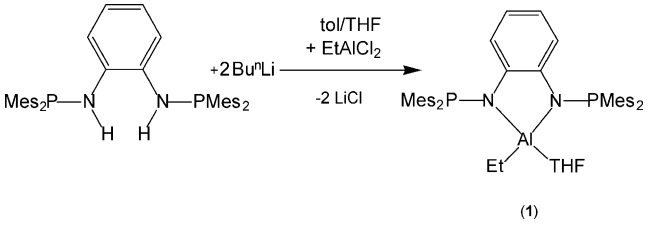
3. Results and discussion

3.1. Synthesis and Spectroscopic Properties of [AlEt(1,2-{N(PMes$_2$)}$_2$C$_6$H$_4$-κ^{2}N,N′)(THF)] (1) and [Mg(1,2-{N(PPh$_2$)}$_2$C$_6$H$_4$-κ^{2}N,N′)(THF)$_2$] (2)

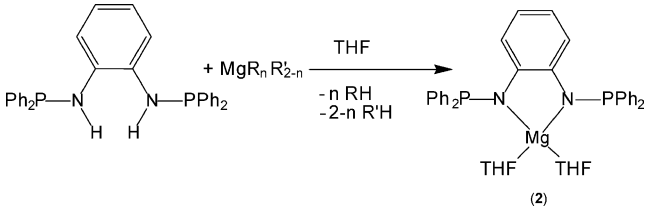
1,2-{NH(PMes$_2$)}$_2$C$_6$H$_4$ [16] is readily deprotonated by two equivalents of Bu^{n}Li in toluene at room temperature to give the dianionic compound [{N(PMes$_2$)}$_2$C$_6$H$_4$]$^{2-}$, which reacts in situ with EtAlCl$_2$ to displace the chloride ligands and give the air- and moisture-sensitive mononuclear complex **1**, as shown in Scheme 2.

1,2-{NH(PPh$_2$)}$_2$C$_6$H$_4$ [17] reacts with MgR$_n$R′$_{2-n}$ (R = butyl, R′ = octyl; n = 1.5) with elimination of the corresponding alkanes and formation of the air- and moisture-sensitive mononuclear complex **2**, as shown in Scheme 3.

In the ^{31}P NMR spectrum, **1** and **2** exhibit a singlet at 27.7 ppm (cf. 24.9 ppm in 1,2-{NH(PMes$_2$)}$_2$C$_6$H$_4$ [16]) and 31.6 ppm (cf. free ligand 32.5 ppm [17]), respectively, which are close to the chemical shifts of the free ligands and thus indicate no interaction of the P atoms with the metal centres. In the ^{1}H NMR spectrum of **1** the Et group on Al is observed at −0.56 ppm (CH$_2$) and 1.03 ppm (CH$_3$), i.e., in the expected range [19]. In the IR spectrum, compounds **1** and **2** show ν(PN) vibrations at 915 and 929 cm^{-1}, which are at higher wavenumbers than those of the free ligands (903 cm^{-1} [16,17]) and indicate a slightly larger N → P back donation in the complex than in the free ligand and also corroborate the ^{31}P NMR shift.



Scheme 2.



Scheme 3.

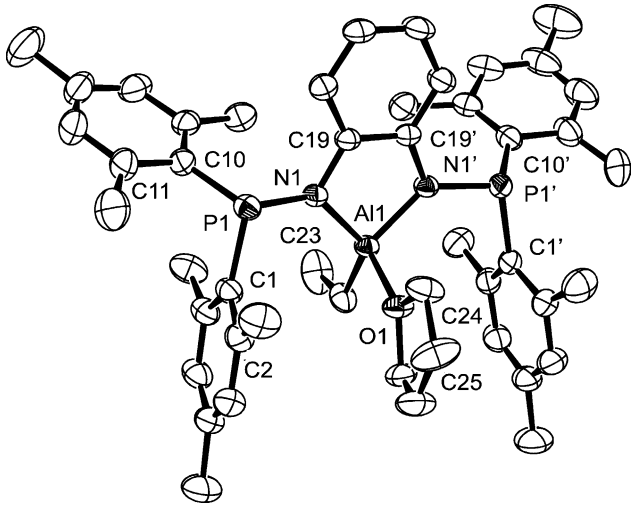


Fig. 2. Molecular structure of **1** (H atoms omitted for clarity; thermal ellipsoids set at 50% probability) [18].

Table 2
Selected bond lengths (Å) and angles (°) for **1**

P(1)–N(1)	1.716(1)	O(1)–Al–C(22)	100.2(1)
Al–N(1)	1.863(1)	C(1)–P(1)–C(10)	105.05(8)
Al–C(22)	1.949(2)	N(1)–P(1)–C(10)	110.49(7)
Al–O(1)	1.899(2)	N(1)–P(1)–C(1)	102.43(6)
N(1)–Al–N(1′)	90.91(8)	P(1)–N(1)–Al	134.25(7)
N(1)–Al–C(22)	126.90(6)	C(19)–N(1)–Al	108.7(1)
N(1)–Al–O(1)	104.54(6)	C(19)–N(1)–P(1)	114.6(1)

3.2. Molecular structure of complexes *1* and *2*

Pale yellow crystals of **1** were obtained from toluene/THF at 4 °C. Compound **1** (Fig. 2) crystallises in the monoclinic space group C2/m, with four molecules of **1** and six non-coordinating toluene molecules in the unit cell. Selected bond lengths and angles are listed in Table 2. Yellow crystals of **2** were obtained from a concentrated THF solution at 4 °C. Compound **2** (Fig. 3) crystallises in the orthorhombic space

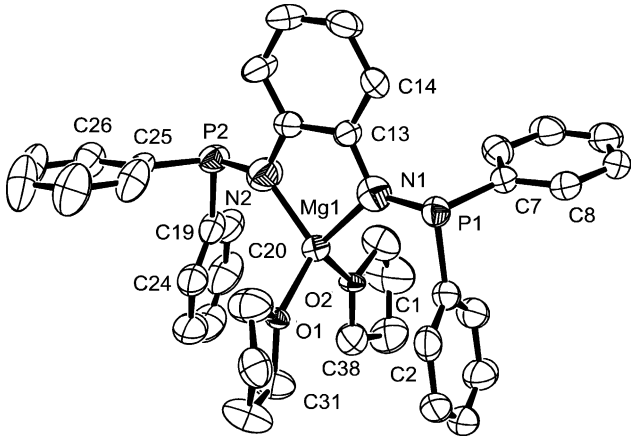


Fig. 3. Molecular structure of **2** (H atoms omitted for clarity; thermal ellipsoids set at 50% probability) [18].

Table 3
Selected bond lengths (Å) and angles (°) for **2**

P(1)–N(1)	1.687(3)	N(1)–P(1)–C(7)	105.2(2)
P(2)–N(2)	1.674(3)	C(1)–P(1)–C(7)	98.5(2)
Mg–N(1)	1.999(3)	N(1)–P(1)–C(1)	100.2(2)
Mg–N(2)	2.011(3)	N(2)–P(2)–C(19)	100.8(2)
Mg–O(1)	2.018(3)	N(2)–P(2)–C(25)	105.4(2)
Mg–O(2)	1.997(3)	C(19)–P(2)–C(25)	96.5(2)
N(1)–Mg–N(2)	86.33(1)	P(1)–N(1)–Mg	130.0(2)
O(1)–Mg–O(2)	107.92(1)	P(2)–N(2)–Mg	132.2(2)
N(1)–Mg–O(2)	112.65(1)	C(18)–N(2)–P(2)	117.2(3)
N(2)–Mg–O(1)	115.85(1)	C(13)–N(1)–P(1)	116.6(3)
C(18)–N(2)–Mg	109.2(2)	C(13)–N(1)–Mg	109.2(2)

group $Pna2_1$, with four molecules in the unit cell. Selected bond lengths and angles are listed in Table 3.

Compounds **1** and **2** are mononuclear and have a five-membered chelate ring formed by coordination of both nitrogen atoms to the metal. The metal atoms in **1** and **2** are coordinated in a distorted tetrahedral fashion by two nitrogen atoms, as well as one ethyl and one THF ligand (for Al) or two THF ligands (for Mg). Compound **1** is located on a symmetry plane with the atom aluminium, a disordered THF ligand and the ethyl group lying on the mirror plane. The N(1)–Al–N(1′) bond angle of 90.91(8)° is smaller than the ideal tetrahedral bond angle of 109.5°. The Al–N(1) bond length of 1.863(1) Å (average bond length of 1.892 Å for four-coordinate Al [20]), is comparable to that in four-coordinate β-diketiminato aluminium alkyl complexes [1.850(2)–1.922(2) Å] [21]. The N(1)–Al–C(22) bond angle of 126.90(6)° is larger than expected, and comparable to the values of 125.97(8) and 126.62(7)° obtained for three-coordinate cationic aluminium alkyl complexes incorporating the β-diketiminato ligand $[AlMe(\{N(R)CMe\}_2CH\text{-}\kappa^2N,N')][B(C_6F_5)_4]$ [22] (R = 2,6-$Pr^i{}_2C_6H_3$). The Al–C(22) bond length of 1.949(2) Å is larger than those of 1.868(4) and 1.872(4) Å observed for similar four-coordinate aluminium alkyl complexes such as $[AlMe(\{N(SiMe_3)CPh\}_2CH\text{-}\kappa^2N,N')(THF)]$ [23]. The Al–O(1) bond length of 1.899(2) Å is close to those of 1.875(3) and 1.887(4) Å observed for the latter complex [23].

The nitrogen atoms are surrounded in a trigonal-planar fashion by C(19), P(1), and Al, and the sum of the bond angles is 357.6°. The P(1)–N(1) bond length of 1.716(1) Å is larger than that of 1.696(1) Å observed in the free ligand [16]. The P(1)–N(1)–Al bond angle of 134.25(7)° is larger than expected, probably due to the chelating effect.

The average Mg–N bond length of 2.005(3) Å is close to those of 2.034(3) and 2.046(3) Å observed in the methoxy-bridged dimeric complex $[Mg(\mu\text{-}OMe)\{1,2\text{-}(NPr^i)_2C_7H_5\text{-}\kappa^2N,N'\}]_2$ [24]. The average Mg–O bond length of 2.008(3) Å is similar to that of 2.066(4) Å observed for the mononuclear complex $[MgMe(\{N(R)CMe\}_2CH\text{-}\kappa^2N,N')(THF)]$ (R = 2,6-$Pr^i{}_2C_6H_3$) [24]. The N(1)–Mg–N(2) bond angle of 86.33(1)° is larger than that of 76.94(12)° observed for the five-membered chelate ring in $[Mg(\mu\text{-}OMe)\{1,2\text{-}(NPr^i)_2C_7H_5\text{-}\kappa^2N,N'\}]_2$ [24]. The nitrogen atoms are surrounded in a trigonal-planar fashion by C(13), P(1)

Table 4
Data for solvent-free polymerisation of ε-caprolactone catalysed by complex **1** at 110 °C

Entry	Monomer:**1**	Time (h)	Conversion (%)	M_n	M_w	PD	Activity (g/mol h)
1	200	0.25	31	11000	32000	2.70	2.9×10^4
2	200	1	100	15000	42000	2.79	2.4×10^4
3	200	7	100	11000	31000	2.77	3.4×10^3
4	400	2	100	21000	36000	1.73	2.4×10^4
5	800	2	36	11000	16000	1.40	1.7×10^4
6	1600	2	7	18000	26000	1.44	6.9×10^3
7	2000	24	100	84000	121000	1.45	9.9×10^3

and Mg(1) (for N(1), sum of bond angles 355.8°) or C(18), P(2) and Mg(1) (for N(2), sum of bond angles 358.6°). The P atoms have a distorted tetrahedral environment in which the C(1)–P(1)–C(7) and C(19)–P(2)–C(25) bond angles of 98.5(2)° and 96.5(2)° have large deviations from the tetrahedral angle of 109.5°, probably due to the steric requirements of the two THF ligands and the lone pair of electrons on the two phosphorus atoms.

3.3. *Polymerisation of ε-caprolactone and β-butyrolactone catalysed by complexes **1**, **2** and [ZnPr{1-N(PMes$_2$)-2-N(PHMes$_2$)C$_6$H$_4$-κ^{2}N,N′}] (**3**)*

When the polymerisation of ε-caprolactone (ε-CL) was catalysed by complex **1** in an ε-caprolactone:catalyst ratio of 200:1 and the reaction is quenched after different amounts of time, similar polydispersities and molecular weights were obtained (Table 4).

This result clearly indicates that, in contrast to complex **3**, there is no increase in the molecular weight of the polymers with time (vide infra). The rather large polydispersity with similar molecular weights indicates that different catalytically active species are participating in the polymerisation (entries 1–3 in Table 4). However, the conversion increases with increasing polymerisation time.

When the monomer:catalyst ratio was increased polymers with higher molecular weights and lower polydispersities (PD, M_w/M_n) can be obtained, but in all cases the number of active sites remains rather small (27%). The ^{13}C NMR spectrum of the polycaprolactone shows that there is no insertion of the monomer into the metal–amide bond, but rather a coordinative pathway in which the anionic ethyl group acts as the initiator by becoming one of the chain end moieties.

A comparison of the catalytic activity of complex **1** in the polymerisation of ε-CL with [AlMe{NR(CH$_2$)$_3$NR-κ*N*,*N*′}] (R = 2,6-Pr$^i_2$C$_6$H$_3$) [12c] shows that the activity of the former is twice the activity of the latter under similar reaction conditions (monomer:catalyst = 200, polymerisation time = 4 h, solvent = toluene). Interestingly, both complexes yielded polycaprolactone with comparable molecular weights and polydispersities.

When the polymerisation of ε-caprolactone was catalysed by **2** in toluene at 110 °C with an ε-caprolactone:catalyst ratio of 1000:1 (Table 5, entry 1) about 33% monomer conversion was achieved in 30 min. When the same monomer:catalyst ratio was used but without solvent (entry 2 in Table 5), a higher activity was observed with 70% conversion. However, the molecular weight of the obtained polymers remained almost constant. Five-fold increase of the ratio (entry 3) resulted in a small decrease in molecular weight, but no change in the conversion was observed. Increasing the ratio to 10,000:1 (entry 4, Table 5) led to substantial decrease in activity to 1.5% conversion, and this indicates that some deactivation of the catalyst, possibly through coordination, takes place at high monomer concentrations.

Table 5
Data for polymerisation of ε-caprolactone catalysed by complex **2** for 30 min at 110 °C

Entry	Monomer:**2**	Solvent	Conversion (%)	M_n	M_w	PD	Activity (g/mol h)
1	1000	Toluene	32.6	6000	9900	1.64	7.45×10^4
2	1000	None	70	6100	8200	1.36	1.62×10^5
3	5000	None	70	5200	7800	1.49	1.26×10^5
4	10000	None	1.5	1000	2400	2.40	3.34×10^4

Table 6
Data for polymerisation of ε-caprolactone and β-butyrolactone catalysed by complex **3**

Entry	Monomer	Monomer:**3**	*t* (h)	*T* (°C)	Conversion (%)	M_n	M_w	PD
1	ε-CL	2000	3	100	65	970500	1312900	1.35
2	ε-CL	2000	0.08	100	59	830	900	1.08
3	ε-CL	200	15	100	100	19050	23750	1.25
4	ε-CL	200	15	85	100	28900	43500	1.50
5	β-BL	200	15	100	100	16000	19500	1.22
6	β-BL	200	15	85	100	17200	21500	1.25

As far as we know, complex **2** is the first magnesium amido complex tested in the polymerisation of ε-CL. A comparison of the catalytic activity of this complex with magnesium alkoxides [9b] reveals that by applying the same monomer:catalyst ratio (5000) complex **2** produces within 30 min PCL with M_n = 5.200 kDa and PD = 1.49 (conversion of 70%), while the magnesium alkoxide yields within 2 h PCL with a lower M_n (2.2 kDa) and a polydispersity of 1.12 (conversion of 86%).

When the polymerisation of ε-caprolactone catalysed by complex **3** was carried out with a large ε-caprolactone:catalyst ratio (2000) the reaction was complete after 3 h and produced a solid polycaprolactone with a polydispersity of 1.35 (entry 1, Table 6). Although a living polymerisation will produce polymers with a M_n of about 230,000 Dalton the formation of polymers with higher M_n and M_w indicates that about 23% of the catalyst is active. The conversion of 65% is attributed to the higher viscosity of the obtained polymer impeding the approach of new monomers to the active centre.

To show whether this activation is operative even in the earliest stages of the polymerisation, the reaction was also quenched after 5 min, after which 59% of the polymer had already been oligomerised to about 7 units of ε-caprolactone (entry 2, Table 6). This result indicates that during the early stages of the polymerisation the entire complex is active for the polymerisation, but chain-transfer mechanisms produce polymers with higher molecular weight and higher polydispersity.

Since in early stages the complex behaves as a living polymerisation catalyst (M_w/M_n = 1.08), it seemed plausible that reducing the amount of ε-caprolactone should allow complete consumption of the monomer with formation of a living polymer in which all the active sites are still active (entry 3, Table 6). Polymerisation at a small ε-caprolactone:catalyst ratio (200) produces a polycaprolactone with a degree of polymerisation close to 200. The higher the reaction temperature the lower the molecular weight of the polymers and the lower the polydispersity (cf. entries 3 and 4, Table 6) due to an increase in chain-termination processes (transesterifications).

Comparison of the catalytic performance of complex **3** in the polymerisation of ε-CL with other well defined Zn complexes bearing N-C-C-N chelating ligands and an additional alkyl group [13b-c] reveals that all the complexes exhibit similar activities. In addition, complex **3** produced the highest molecular weight polymer (entry 1, Table 6) as compared to other Zn systems.

While complex **1** was found to be inactive in the polymerisation of β-butyrolactone (β-BL), complex **3** exhibits a similar activity towards β-butyrolactone as for ε-caprolactone, producing poly(3-hydroxybutyrate) with similar degree of polymerisation (Table 6). Interestingly, for both monomers we found that the polymerisation produces polymers with a propyl group at one end of the chain, which indicates that in the ring-opening polymerisation with complex **3** transfer of the propyl group to the monomer starts the polymerisation.

4. Conclusion

In conclusion, we have presented a new family of moisture-sensitive Al, Zn and Mg bisamido complexes that can effectively be used for the rapid polymerisation of lactones to polyesters, in some cases in a living fashion.

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