Zinc(II), Samarium(III) and Tin(II) Complexes Featuring a Tridentate Nitrogen Donor for the Ring-Opening Copolymerization of (D,L)-Lactide and Glycolide

Anca Dumitrescu,[a] Blanca Martin-Vaca,[a] Heinz Gornitzka,[a] Jean-Bernard Cazaux,[a] Didier Bourissou,*[a] and Guy Bertrand*[a,b]

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The synthesis, structure, and catalytic activity in ring-opening polymerization of zinc(II), samarium(III) and tin(II) complexes featuring a tridentate nitrogen donor are described.

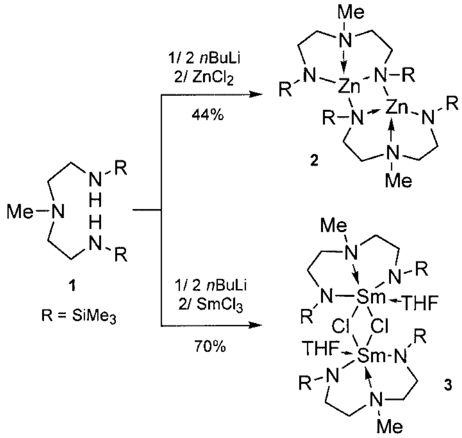
Introduction

The design of discrete metal complexes that could be highly active and selective catalysts for the polymerization of a variety of monomer classes is of considerable current interest.[1] A significant aim is to construct less expensive catalysts while retaining the benefits of discrete metal complexes. These goals are especially important with respect to the copolymerization of lactide (L) and glycolide (G), to give poly(lactide-*co*-glycolide) (PLGA), biodegradable and biocompatible polyesters that are garnering great interest due to their biomedical, pharmaceutical, and agricultural applications.[2] To this end complexes of various metals (aluminum,[3−5] tin,[6] zinc,[7−9] iron,[10] magnesium,[7d] zirconium[11]) and lanthanides (yttrium,[12,13] lanthanum,[12,13] samarium,[13] ytterbium[13]) have been studied.

Chelating nitrogen ligands are often used for stabilizing low-valent species.[14] We have recently shown that diamidoamino ligands $[(RNCH_2CH_2)_2NR']^{2-}$, initially developed by Cloke,[15] are particularly well adapted for the stabilization of neutral as well as cationic group 13 Lewis acids.[3] Due to the formation of a rather rigid bicyclic core, these tridentate nitrogen donors enforce an approximately trigonal-monopyramidal coordination geometry around the metal, and the ensuing empty axial coordination site has been used for promoting the ring-opening polymerization of heterocycles such as propylene oxide and (D,L)-lactide.[3] We have also shown that stannylenes featuring diamidoamino ligands are monomers both in solution and in the solid state.[16] Here we report the synthesis and structural investigation of related zinc(II) and samarium(III) derivatives which adopt dimeric structures in the solid state. The catalytic activities of the zinc, samarium and previously reported tin complexes for the ring-opening copolymerization of (D,L)-lactide and glycolide are compared.

Results and Discussion

Deprotonation of the triamine **1**[3] with two equivalents of *n*BuLi and treatment of the ensuing dilithium salt with anhydrous $ZnCl_2$ and $SmCl_3$ affords the neutral complexes **2** and **3** in 44 and 70% yield, respectively (Scheme 1).



Scheme 1. Synthesis of compounds **2** and **3**

The dimeric structure of **2**, both in solution and in the solid state, was demonstrated by the presence of two sets of signals for the $SiCH_3$ groups in the ^1H and ^{13}C NMR spec-

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[a] Laboratoire d'Hétérochimie Fondamentale et Appliquée du CNRS (UMR 5069), Université Paul Sabatier,
118, route de Narbonne, 31062 Toulouse Cedex 04, France
Fax: (internat.) + 33-5/6155-8204

[b] UCR-CNRS Joint Research Chemistry Laboratory (UMR 2282), Department of Chemistry − University of California, Riverside, CA 92521−0403, USA
Fax: (internat.) +1-909/787-2725
E-mail: gbertran@mail.ucr.edu

tra and by an X-ray analysis (single crystals were obtained in pentane at −30 °C) (Figure 1). Derivative **2** contains a central rectangular $(Zn-N)_2$ four-membered ring, which is centered on the crystallographically imposed inversion center of the molecule. The Zn1−N2 [2.238(5) Å] and Zn1−N3 [1.907(0) Å] distances are in the typical range for dative (2.10−2.40 Å) and covalent (1.80−1.90 Å) Zn−N bonds,[17] respectively, while the Zn1−N1 [2.105(4) Å] and Zn1−N1a [2.025(2) Å] distances are, as expected, half-way between covalent and dative bonds. Since Zn−N and Sn−N bond lengths are very similar,[17,18] and since secondary bulky amines normally guarantee monomeric structures for both homoleptic zinc and tin amides, the dimeric structure adopted by **2** is rather surprising. It probably results from the geometry enforced by the diamidoamino ligand, which is certainly more adapted for a bent stannylene[18] than for a linear, allenic-type zinc derivative.[17]

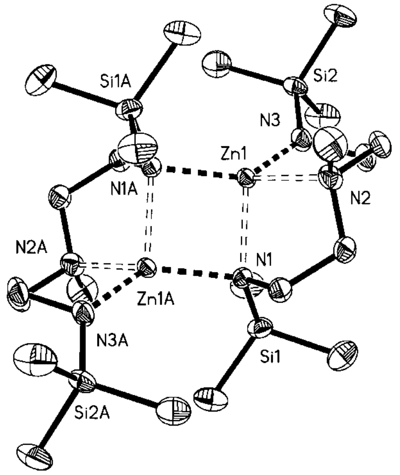

Figure 1. Molecular structure of **2** in the solid state; the hydrogen atoms are omitted for clarity; selected bond lengths (Å) and angles (°): Zn1−N1 2.105(2), Zn1−N1A 2.025(2), Zn1−N2 2.238(2), Zn1−N3 1.907(2), N1−Si1 1.736(2), N3−Si2 1.694(2); N1−Zn1−N2 85.25(6), N1−Zn1−N3 124.48(7), N1−Zn1−N1A 92.49(6), N2−Zn1−N3 86.96(7), N2−Zn1−N1A 127.35(6), N3−Zn1−N1A 133.36(6)

Complex **3** also adopts a dimeric structure but the two $[(Me_3SiNCH_2CH_2)_2NMe]Sm(THF)$ units are bridged by two chlorine atoms (Figure 2). As observed in $[(Cy_2N)_2Sm(\mu\text{-}Cl)(THF)]_2$,[19] the amido nitrogens are in a trigonal planar environment and the $(Sm-Cl)_2$ core is perfectly planar. However, each samarium atom is hexacoordinate and has a strongly distorted octahedral geometry. In other words, the coordination of the amino nitrogen to the lanthanide center does not prevent the coordination of a THF molecule: this is of particular interest for ring-opening polymerization via a coordination-insertion mechanism.[20]

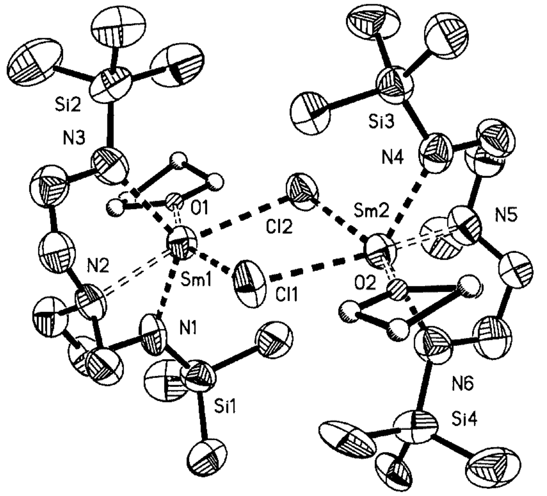

Figure 2. Molecular structure of **3** in the solid state; the hydrogen atoms are omitted for clarity; selected bond lengths (Å) and angles (°): Sm1−Cl1 2.773(3), Sm1−Cl2 2.797(3), Sm1−N1 2.290(12), Sm1−N2 2.574(9), Sm1−N3 2.299(12), Sm1−O1 2.519(8), N1−Si1 1.678(12), N3−Si2 1.695(12); N1−Sm1−N2 68.9(3), N1−Sm1−N3 124.1(4), N1−Sm1−Cl1 104.0(3), N1−Sm1−Cl2 122.1(3), N1−Sm1−O1 83.2(4), Cl1−Sm1−Cl2 75.65(9)

The zinc, samarium and tin derivatives **2−4** initiate the bulk copolymerization of (D,L)-lactide and glycolide (Table 1). As estimated from ^1H NMR spectroscopy, complete conversion of both monomers requires about 3 h at 180 °C with the zinc complex **2**. Copolymers possessing higher molecular weight could be obtained by increasing the reaction time but at the expense of the molecular weight distribution (from 2.3 to 3.6) (entries 1−3). However, high-molecular weight copolymers with narrow distribution and various glycolide contents could be prepared by optimizing the reaction conditions (entries 4 and 5). With the samarium derivative **3**, high conversions of both monomers are observed after only 30 minutes at 180 °C and even 160 °C (entries 6 and 7). When carrying out the copolymerization of a stoichiometric mixture of (D,L)-lactide and glycolide at 160 °C, using **3** as the initiator, a copolymer of high molecular weight and narrow molecular distribution (M_n = 26.200, M_w/M_n = 1.8) was obtained after 3.5 h (entry 9). The tin derivative $[MeN(CH_2CH_2NSiMe_3)_2]Sn$ (**4**)[16] is even more active. Conversions higher than 95% are obtained after only 30 minutes at 180 °C. Upon increasing the reaction time, the molecular weight progressively decreases, while the molecular weight distribution increases, probably due to transesterification reactions (entries 10−12).[21] At 140 °C (entries 13−15), these side reactions are significantly reduced, while the tin catalyst remains very active (conversions higher than 90% after 20 minutes); under these conditions, very high molecular weight copolymers are obtained (M_n = 85.150, M_w/M_n = 1.9) (entry 14).

Conclusion

Since the electronic and steric properties of the ligand can be tuned easily, metal complexes of type **2−4** are promising candidates for ring-opening polymerization of heterocycles,[22] as well as for the metal-organic vapor phase epitaxy (MOVPE)[23] and metal-organic chemical vapor deposition (MOCVD).[24]

Table 1. Bulk copolymerization of (D,L)-lactide and glycolide

Entry	Catalyst	Temp. (°C)	Time (min.)	L/cat.[a]	G/cat.[a]	Conv. L[b] (%)	Conv. G[b] (%)	G/(G+L)[b] (mol %)	M_n [c]	M_w/M_n[c]
1	**2**	180	30	800	342	31	90	55	9.200	2.3
2	**2**	180	80	800	342	76	100	48	17.200	2.7
3	**2**	180	180	800	342	98	100	38	13.000	3.6
4	**2**	180	120	580	249	87	100	34	24.900	1.9
5	**2**	180	140	702	398	79	96	49	39.400	1.7
6	**3**	180	30	130	55	86	100	33	17.800	1.7
7	**3**	160	30	130	55	71	100	39	25.650	1.6
8	**3**	160	60	150	150	44	100	58	16.600	1.7
9	**3**	160	210	150	150	96	100	51	26.200	1.8
10	**4**	180	30	800	342	95	100	30	25.800	2.8
11	**4**	180	60	800	342	96	100	30	21.100	2.9
12	**4**	180	120	800	342	99	100	27	17.700	3.0
13	**4**	140	10	800	342	85	100	32	94.450	1.8
14	**4**	140	20	800	342	93	100	31	85.150	1.9
15	**4**	140	120	800	342	97	100	30	67.100	2.2

[a] Molar ratio. [b] Obtained from ^{1}H NMR spectroscopy. [c] Obtained from GPC analysis by using polystyrene standards.

Experimental Section

General: All reactions were performed under argon atmosphere using standard Schlenk tube techniques. Solvents were dried by standard procedures and distilled prior to use. Amine **1** was prepared according to a literature procedure.[3b] ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AC250 spectrometer. ^{1}H and ^{13}C{^{1}H} chemical shifts are reported in ppm relative to Me_4Si as an external standard.

{[MeN($CH_2CH_2NSiMe_3$)$_2$]Zn}$_2$ (2): An ether suspension (5 mL) of $ZnCl_2$ (0.58 g, 4.3 mmol) was added at −78 °C to an ether solution (10 mL) of the dilithium salt of *N*-methyl-*N*′,*N*′′-bis(trimethylsilyl)-diethylenetriamine (**1**) (4.3 mmol). The solution became yellow, and was allowed to warm to room temperature. After stirring overnight, removal of the solvent under vacuum and extraction with pentane (25 mL), colorless crystals of **2** were obtained at −20 °C. Yield 0.6 g (44%); m.p. 239 °C (dec.). ^{1}H NMR (250 MHz, C_6D_6): δ = 0.25 (s, 18 H, $SiCH_3$), 0.30 (s, 18 H, $SiCH_3$), 1.68−1.62 (m, 2 H, CH_2), 2.03 (m, 4 H, CH_2), 2.11 (s, 6 H, NCH_3), 2.3−2.1 (m, 2 H, CH_2), 2.98 (m, 4 H, CH_2), 3.05 (m, 4 H, CH_2) ppm. ^{13}C{^{1}H} NMR (62.9 MHz, C_6D_6): δ = 3.2 ($SiCH_3$), 3.3 ($SiCH_3$), 44.5 (NCH_3), 47.6 (CH_2), 47.7 (CH_2), 60.3 (CH_2), 65.9 (CH_2). $C_{11}H_{29}N_3Si_2Zn$ (324.9): calcd. C 40.66, H 9.00, N 12.93; found C 40.28, H 9.35, N 12.71.

{[($Me_3SiNCH_2CH_2$)$_2$NMe]Sm(THF)Cl}$_2$ (3): A THF suspension (5 mL) of $SmCl_3$ (1.2 g, 4.7 mmol) was added at −78 °C to a tetrahydrofuran solution (10 mL) of the dilithium salt of **1** (4.7 mmol). The solution was allowed to warm to room temperature and stirred for 4 hours. After removal of the solvent under vacuum and extraction with toluene (5 mL), colorless crystals of **3** were obtained at −20 °C. Yield 1.7 g (70%); m.p. 173 °C (dec.). $C_{15}H_{37}ClN_3OSi_2Sm$ (517.5): calcd. C 34.82, H 7.21, N 8.12; found C 34.65, H 7.53, N 7.91.

X-ray Crystallography: Data for both structures were collected at low-temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation. The structures were solved by direct methods using SHELXS-97[25] and refined with all data on F^2 using SHELXL-97.[26] All non-hydrogen atoms were treated anisotropically. The hydrogen atoms were geometrically idealized and refined using a riding model.

2: Monoclinic, space group $P2_1/n$; T = 173 K; a = 11.668(2), b = 11.300(2), c = 13.894(2) Å; β = 111.67(2)°; V = 1702.4(5) Å^3; Z = 4; R [$I > 2\sigma(I)$] = 0.0241, $wR2$ (all data) = 0.0646 for 2598 unique reflections, 161 parameters, GooF = 1.004.

3: Orthorhombic, space group *Pbca*; T = 173 K; a = 13.184(1), b = 18.567(2), c = 38.049(3) Å; V = 9313.9(14) Å^3; Z = 16; R [$I > 2\sigma(I)$] = 0.0543, $wR2$ (all data) = 0.1453 for 6051 unique reflections, 451 parameters, GooF = 0.820.

CCDC-183554 (**2**) and -183555 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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