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Well-defined, solvent-free cationic barium complexes: Synthetic strategies and catalytic activity in the ring-opening polymerization of lactide

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ABSTRACT

Well-defined, solvent-free cationic barium complexes of the type $[\{L_nX\}Ba]^+\cdot[H_2N\{B(C_6F_5)_3\}_2]^-$ stabilized by multidentate amino-ether phenoxide or fluorinated amino-ether alkoxide ligands $\{L_nX\}^-$ are available according to original, general and high-yield protocols. These cations have been prepared by (i) hydrolysis of heteroleptic complexes $\{L_nX\}BaN(SiMe_2H)_2$ stabilized by Ba···H–Si interactions with $[H(OEt_2)_2]^+\cdot[H_2N\{B(C_6F_5)_3\}_2]^-$, or (ii) reaction of $\{Ba[N(SiMe_2H)_2]_2\}_n$ with the doubly acidic pro-ligands $[\{L_nX\}HH]^+\cdot[H_2N\{B(C_6F_5)_3\}_2]^-$. The solid-state structures of $[\{LO^2\}Ba(THF)_2]^+\cdot[H_2N\{B(C_6F_5)_3\}_2]^-$ ($\{LO^2\}$H = 2-[(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)methyl]-4,6-*di*-*tert*-butylphenol) and $[\{RO^2\}Ba]^+\cdot[H_2N\{B(C_6F_5)_3\}_2]^-$ $\{RO^2\}$H = 2-[(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)methyl]-1,1,1,3,3,3-hexafluoropropan-2-ol) are described, highlighting the key role of internal secondary Ba···F–C interactions in these highly electrophilic species. In combination with an excess of an external nucleophile (chosen from benzyl alcohol, 1,3-propanediol, benzyl amine or an hydroxyl-functionalized alkoxy-amine) as a co-initiator, some of these Ba cations provide extremely efficient catalysts for the immortal ring-opening polymerization of L-lactide in the temperature range 0–30 °C, converting rapidly up to 5000 equiv. of monomer in a controlled fashion and with excellent end-group fidelity.

1. Introduction

The polymerization of enantiomerically pure L-lactide (L-LA), a fully bio-resourced monomer derived from the fermentation of sugars or starch [1], has attracted a great deal of attention since the turn of the century, not least because poly(L-lactide) (PLLA) is a biodegradable thermoplastic with mechanical properties comparable to those of polystyrene [2]. A broad range of well-defined $\{L_nX\}$Met–Nu complexes (where $\{L_nX\}^{n-}$ is a bulky ancillary ligand and Nu^- is a reactive nucleophilic group such as alkyl, amide or alkoxide) have been developed for the controlled ring-opening polymerization (ROP) of L-LA [3,4]. Many initiators based on zinc [5], aluminum [6] or group III and lanthanide metals [7] allow for the living ROP of L-LA, as well as that of other cyclic esters such as *rac*-lactide (the equimolar mixture of the D- and L-isomers of lactide), ε-caprolactone and β-butyrolactone [8], and a good understanding of ROP by coordination-insertion mechanism was gained through the use of these initiators. Magnesium complexes are also known to be competent ROP initiators [3,5b,9], but because of their higher sensitivity they are comparatively less common than their Zn analogues. The development of catalytic systems for the *immortal* ROP (*i*ROP) of cyclic esters, first proposed by Inoue for the ROP of epoxides [10], represents one of the persisting challenges in this field: whereas a living system generates only one polymer chain *per* metal, the use of an excess of external protic co-initiator (typically an alcohol) with the metal initiator enables the production of hundreds of polymer chains *per* metal center [11]. Besides, we and others have recently demonstrated that cationic well-defined complexes, with their exacerbated Lewis acidity, promoted the polymerization of cyclic esters with great efficacy and were worth considering as a new generation of ROP catalysts [12–16].

In stark contrast with Zn or even Mg, only a handful of efficient ROP single-site initiators based on the larger alkaline-earth metals (calcium, strontium and barium) have been reported to date [5f,16–18]. Chisholm et al. pioneered the first effective calcium initiators supported by highly encumbered *tris*(pyrazolyl)borate and β-diketiminate ancillary ligands [17c–d], while Feijen et al. showed that $Ca[N(SiMe_3)_2]_2(THF)_2$ [18a] and the dimeric $\{Ca(THF)\}_2(thmd)_2(\mu\text{-}thmd)(\mu\text{-}N(SiMe_3)_2$ (thmd-H = tetramethylheptanedione) [17a] also constituted moderately active initiators. Hill and co-workers reported the syntheses of stable heteroleptic *bis*(phosphinimino)methyl derivatives of Ca and Sr which showed promising ROP catalytic ability [17b], but surprisingly they did not elaborate on these initial results. If two other examples of ill-defined Sr compounds able to promote the ROP of cyclic esters have been reported [19], the only molecular Ba ROP initiator known until very recently was the amine*bis*(phenolate) complex disclosed by Davidson et al. [18d].

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Such paucity of well-defined Ae-based initiators (Ae = Ca, Sr, and Ba) is undoubtedly related to the difficulties encountered in taming the high reactivity of these very large (r_{ionic} = 1.00, 1.18 and 1.35 for Ca, Sr and Ba, respectively) [20] and electropositive metals. This is especially the case with the largest element, barium. Due to their high kinetic lability, the preparation of stable heteroleptic complexes {L_nX}Ba–Nu (where {L_nX}$^-$ is a monoanionic ancillary ligand) is very troublesome, as their synthesis is often hampered by deleterious Schlenk-type equilibria. Starting from {L_nX}Ba–Nu, these side-reactions lead to the formation of aggregates and poorly reactive species such as {L_nX}$_2$Ba and {BaNu$_2$}$_n$. As the pronounced ionic nature of the bonding increases with the ionic radius of the element, the propensity for ligand scrambling is most detrimental in the case of Ba complexes. For instance, heteroleptic complexes of Ca and Sr supported by *bis*(phosphinimino)methyl [17b] or β-diketiminate ligands [21] are stable, but the same is not true of their Ba parents.

Efficient ROP initiators based on Ae metals (and especially Ba) can only be developed if convenient strategies aimed at stabilizing heteroleptic complexes against ligand scrambling are devised. Although steric bulk can sometimes impart sufficient stability to the complexes [17b,22], it is hard to rationalize it for all ligand frameworks, especially as the size of the metal varies considerably from Ca to Ba. Hill and co-workers reported an interesting strategy based on the dearomatization of bulky aromatic ligands [23]. Methods relying on stabilization by internal secondary interactions seemed to us to offer real scope as a general way to stabilize labile Ae species. We have recently described Ae[N(SiMe$_2$H)$_2$]$_2$(THF)$_x$ homoleptic precursors (Ae = Ca, x = 1; Sr, x = 0.66; Ba, x = 0), and showed that the presence of internal stabilizing β-Si–H agostic interactions constituted a key factor in the isolation of the heteroleptic complexes {L_nX}Ae–N(SiMe$_2$H)$_2$ [17h]. Besides, we have also shown that the extremely electrophilic cations in {RO}Ae$^+$·X$^-$ ion pairs (where {RO}$^-$ is a tertiary fluorinated alkoxide and X$^-$ is a weakly-coordinating anion) were stabilized by internal Ae···F–C secondary interactions in the solid-state [16c].

In the present study, the syntheses and solid-state structures of discrete cationic complexes of barium supported by bulky amino-ether phenoxide and alkoxide ligands are described. A synthetic strategy for the isolation of such cations is detailed, and cases of Ba···H–Si and Ba···F–C secondary interactions in charge-neutral and cationic complexes are discussed. The remarkable catalytic activity of these cations in the *immortal* ROP of L-LA is also presented.

2. Experimental

2.1. General procedures

All manipulations were performed under inert atmosphere using standard Schlenk techniques or in a Jacomex glove-box (O_2 < 1 ppm, H_2O < 5 ppm) for catalyst loading.

NMR spectra were recorded on Bruker AC-300, AC-400 and AM-500 spectrometers. All chemicals shifts were determined using residual signals of the deuterated solvents and were calibrated versus $SiMe_4$. Assignment of the signals was carried out using 1D (^{1}H, ^{13}C{^{1}H}) and 2D (COSY, HMBC, and HMQC) NMR experiments. Coupling constants are given in Hertz. ^{19}F{^{1}H} chemical shifts were determined by external reference to an aqueous solution of $NaBF_4$. ^{11}B chemical shifts are reported relative to BF_3·Et_2O.

Size Exclusion Chromatography (SEC) measurements were performed on a Polymer Laboratories PL-GPC 50 instrument equipped with a PLgel 5 Å MIXED-C column and a refractive index detector. The GPC column was eluted with THF at room temperature at 1 mL/min and was calibrated using 11 monodisperse polystyrene standards in the range of 580–380 000 g mol^{-1}. The molecular weights of all poly(lactide)s were corrected by the recommended factor of 0.58 [24].

MALDI-ToF-MS spectra were obtained with a Bruker Daltonic MicroFlex LT, using a nitrogen laser source (337 nm, 3 ns) in linear mode with a positive acceleration voltage of 20 kV. Samples were prepared as follow: 1 μL of a 2:1 mixture of a saturated solution of α-cyano-4-hydroxycinnamic acid (Bruker Care) in HPLC quality acetonitrile and a 0.1% solution of trifluoroacetic acid in ultrapure water was deposited on the sample plate. After total evaporation, 1 μL of a 5 to 10 mg mL^{-1} solution of the polymers in HPLC-quality THF were deposited. Bruker Care Peptide Calibration Standard and Protein Calibration Standard I were used for external calibration.

Elemental analyses were performed on a Carlo Erba 1108 Elemental Analyser instrument at the London Metropolitan University by Stephen Boyer and were the average of a minimum of two independent measurements.

FTIR spectra were recorded at room temperature as Nujol mulls in KBr plates on a Shimadzu Affinity-IR spectrometer.

2.2. Materials

Benzyl alcohol (VWR) and 1,3-propanediol (Acros) were dried and distilled over dry magnesium turnings and then stored over activated 3 Å molecular sieves. Benzyl amine (Acros) was distilled from CaH_2 and kept over molecular sieves. BaI_2 (anhydrous beads, 99.995%) was purchased from Aldrich and used as received. 1-Aza-15-crown-5 (IBC) and 3,3,3-trifluoro-2-(trifluoromethyl)-1,2-propenoxide (Apollo) were used without purification. HN(SiMe$_3$)$_2$ (Acros) and HN(SiMe$_2$H)$_2$ (ABCR) were dried over activated 3 Å molecular sieves and distilled under reduced pressure prior to use. Technical grade L-lactide (provided by Total Petrochemicals) was purified by recrystallization from a hot, concentrated *i*PrOH solution (80 °C), followed by two subsequent recrystallizations in hot toluene (105 °C). After purification, L-lactide was stored at −30 °C under the inert atmosphere of the glove-box. Toluene was distilled under Argon from melted sodium prior to use. THF was first pre-dried over sodium hydroxide and distilled under argon over CaH_2, and then freshly distilled a second time under argon from Na/benzophenone prior to use. Et_2O, dichloromethane and pentane were distilled under argon from Na/benzophenone, CaH_2 and Na/benzophenone/tetraglyme, respectively. All deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampoules over activated 3 Å molecular sieves and were thoroughly degassed by several freeze–thaw cycles.

The synthetic precursors [H(OEt$_2$)$_2$]$^+$·[H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$ [25], Ba[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ [26], [{LO^1}HH]$^+$·[H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$ [16c] and {Ba[N(SiMe$_2$H)$_2$]$_2$}$_n$ [17h], the complexes [{LO^2}Ba]$^+$·[H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$ (**5**) [16a] and [{RO^2}Ba]$^+$·[H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$ (**6**) [16c], and the pro-ligands {LO^1}H [5j], {LO^2}H [5j] and {RO^2}H [16c] were all prepared as described elsewhere.

2.3. Syntheses and characterization

2.3.1. Synthesis of {LO^1}BaN(SiMe$_3$)$_2$ (*1*)

At room temperature, a solution of {LO^1}H (0.25 g, 0.71 mmol) in Et_2O (5 mL) was slowly added to a solution of Ba[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ (0.45 g, 0.75 mmol) in Et_2O (10 mL). A white precipitate formed instantly. The suspension was stirred for 2 h, and the supernatant was eliminated by filtration to afford **1** as white powder after drying *in vacuo*. Yield 0.38 g (83%). ^{1}H NMR (C_6D_6, 298 K, 500.13 MHz): δ 7.54 (d, $^4J_{HH}$ = 2.2 Hz, 1H, *m*-H), 7.06 (d, $^4J_{HH}$ = 2.2 Hz, 1H, *m*-H), 3.30 (s, 2H, Ar–C*H*$_2$–N), 3.58–2.89 (br, 10H, CH$_2$–C*H*$_2$–O and 6H, O–C*H*$_3$), 2.21 (br, 4H, N–C*H*$_2$–CH$_2$), 1.69 (s, 9H, *o*-C(C*H*$_3$)$_3$), 1.42 (s, 9H, *p*-C(C*H*$_3$)$_3$), 0.14 (d, $^4J_{HH}$ = 3.0 Hz, 18H, Si(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 298 K, 125.76 MHz): δ