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Stable Divalent Germanium, Tin and Lead Amino(ether)-phenolate Monomerik^{iew Article Online} DOI: 10.1039/C3DT51681D Complexes: Structural Features, Inclusion Heterobimetallic Complexes, and ROP Catalysis

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Abstract

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Stable germanium(II) and lead(II) amido complexes $\{LO^i\}M(N(SiMe_3)_2)$ (M = Ge^{II}, Pb^{II}) bearing amino(ether)phenolate ligands are readily available using the proteo-ligands $\{LO^i\}H$ of general formula 2-CH₂NR₂-4,6-*t*Bu₂-C₆H₂OH (i = 1, NR₂ = N((CH₂)₂OCH₃)₂; i = 2, NR₂ = NEt₂; i = 3, NR₂ = aza-15-crown-5) and M(N(SiMe₃)₂)₂ precursors. The molecular structures of these germylenes and plumbylenes, as well as those of $\{LO^3\}GeCl, \{LO^3\}SnCl$ and of the congeneric $\{LO^4\}Sn^{II}(N(SiMe_3)_2)$ where NR₂ = aza-12-crown-4, have been determined crystallographically. All complexes are monomeric, with 3-coordinate metal centres. The phenolate systematically acts as a N^O_{phenolate} bidentate ligand, with no interactions between the metal and the $O_{side-arm}$ atoms in these cases (for $\{LO^1\}^-, \{LO^3\}^-$ and $\{LO^4\}^-$) where they could potentially arise. For each family, the lone pair of electrons essentially features ns^2 character, and there is little, if any, hybridization of the valence orbitals. Heterobimetallic complexes $\{LO^3\}M(N(SiMe_3)_2)$: LiOTf, where the Li^+ cation sits inside the tethered crownether, were prepared by reaction of $\{LO^3\}M(N(SiMe_3)_2)$ and LiOTf (M = Ge^{II}, Sn^{II}). The inclusion of Li⁺ (featuring close contact with the triflate anion) into the macrocycle bears no influence on the coordination sphere of the divalent tetrel element. In association with iPrOH, the amido germylenes, stannylenes and plumbylenes catalyse the controlled polymerisation of L- and racemic lactide. The activity increases linearly according to $Ge^{II} \ll Sn^{II} \ll Pb^{II}$. The simple germylenes generate very sluggish catalysts, but the activity is significantly boosted if the heterobimetallic complex $\{LO^3\}Ge(N(SiMe_3)_2)$ ·LiOTf is used instead. On the other hand, with 10-25 equiv of *i*PrOH, the plumbylenes afford highly active binary catalysts, converting 1,000 or 5,000 equiv of monomer at 60 °C within 3 or 45 min, respectively, in a controlled fashion.

Poly(L-lactide) is a biopolymer used for a variety of specialty applications and as a bulk polymer.¹ It is conveniently prepared through metal-mediated ring-opening polymerisation (ROP) of L-lactide. Following a decade of intense research, a great diversity now exists in the range of metal catalysts available for ROP reactions and related ring-opening processes,² with zinc,³ aluminium⁴ and rare-earth elements⁵ attracting the most interest.⁶ Industrial plants still rely on the use of simple tin(II) systems such as the versatile tin(II) *bis*(octanoate),⁷ an inexpensive and robust compound considered safe by the US Food and Drug Administration. Considering the popularity of this and other group 14 polymerisation catalysts,⁸ it is surprising that only a handful of germanium(II),⁹ tin(II)^{6e-g,10} or even lead(II)¹¹ ROP catalysts have been reported.¹² The canon of ligands employed to tailor ROP catalysts is virtually boundless, with prominent examples including bulky β -diketiminates or a range of phenolate (salen, salan, amino-phenolates...) ligands.²⁻⁶ We embarked a few years ago upon the design of ROP catalysts built on somewhat unconventional metals supported by multidentate amino(ether)-phenolate ligands,^{6j,6l,13} and explored ROP mechanisms using tin(II) complexes.^{6g,14} In the course of these investigations, we became involved in the coordination chemistry of tin(II) and related germanium(II) and lead(II) amino(ether)-phenolate complexes.

Phenolates are amenable to the tuning of their electronic and steric properties through modification of the substituents at the *ortho* and *para* positions of the aromatic ring, and this has led to a rich coordination chemistry.¹⁵ Yet, phenolates have seldom been applied to the stabilisation of singlet germylene, stannylene or plumbylene species, the heavier homologues of divalent carbenes.¹⁶ Unlike alkoxide M(OR)₂ species that are often polymetallic (R = alkyl),¹⁷ sterically stabilised (and significantly less basic) homoleptic M(OAr)₂ phenolate complexes are monomeric for M = Ge and Sn (Ar = 2,6-*t*Bu₂-4-MeC₆H₂¹⁸ or 2,6-

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Mes₂C₆H₃¹⁹). On the other hand, structural information for analogous plumbylenes are subpredice online and it is just recently that the monomeric Pb(OC₆H₃-2,6-(2,6-*i*Pr₂C₆H₃)₂)₂ has been authenticated in the solid state.²⁰ The presence of side-arms containing heteroatoms (N, O) is a contributing factor towards the kinetic stability of three- or four-coordinate divalent homoleptic complexes formed through intramolecular coordination of the heteroatom(s) onto the metal centre.²¹ Tetracoordinated complexes (N^O)₂M supported by chelating dimethylaminoethoxide or 2,4,6-tris[(dimethylamino)methyl]phenolate ligands were found to be monomeric for M = Ge, Sn,²² but the solid-state structure of the lead(II) derivative was not available.²³ The bidentate 2-[(dimethylamino)methyl]phenolate yielded the monomeric germylene (N^O)₂Ge, but the tin(II) and Pb(II) derivatives could not be structurally characterised; the parent heteroleptic complex (N^O)SnCl was dimeric, with O_{phenolate} atoms bridging two four-coordinate tin(II) centres.²⁴ Dimers are commonly observed for tin(II) when the germanium analogues are monomeric (lead congeners are seldom mentioned), *e.g.* in {M(OCH₂CH₂NMe₂)(N(SiMe₃)₂)_n (M = Ge, n = 1; M = Sn, n = 2).²⁵

We report here the synthesis and characterisation of monomeric, heteroleptic, 3coordinate complexes of germanium(II), tin(II) and lead(II) incorporating multidentate, monoanionic amino(ether)-phenolate ligands, and their behaviour towards the ROP of Llactide is introduced. Heterobimetallic complexes prepared by inclusion of alkali salts in the side-arm of these ligands containing an aza-crown-ether side-arm are also presented.

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Stable, monomeric divalent metal aminophenolates

Results and Discussion

The heteroleptic amido complexes $\{LO^1\}M(N(SiMe_3)_2)$ (M = Ge, 1; Sn, 5; Pb, 9), $\{LO^2\}M(N(SiMe_3)_2)$ (M = Ge, 2; Sn, 6; Pb, 10), $\{LO^3\}M(N(SiMe_3)_2)$ (M = Ge, 3; Sn, 7; Pb, 11) and $\{LO^4\}M(N(SiMe_3)_2)$ (M = Sn, 8) where the metal is supported by a monoanionic chelating ligand chosen from an amino(ether)-phenolate (as in $\{LO^1\}^-$), an amino-phenolate (as in $\{LO^2\}^-$) or an amino(crown-ether)-phenolate (as in $\{LO^3\}^-$ and $\{LO^4\}^-$) are available in good isolated yields upon protonolysis of the homoleptic divalent metal-amido precursors $M(N(SiMe_3)_2)_2$ with the corresponding proteo-ligand $\{LO^i\}H$ in diethyl ether (Scheme 1).²⁶



Scheme 1. Synthesis of the germylenes, stannylenes and plumbylenes **1–11**; complexes **5–7** are taken from references 6*g* and 14*a*.

The convenient protonolysis procedure offered better yields than one-pot salt View Article Online DOI: 10.1039/C3DT51681D metathesis reactions.²⁷ For instance, the germylene **3** was isolated after a tedious work-up in only 46% yield from the one-pot reaction of $\{LO^3\}H$, $GeCl_2$ ·dioxane and two equiv of $KN(SiMe_3)_2$. The stoichiometric reaction of $\{LO^3\}$ GeCl (a colourless solid accessible upon treatment of $GeCl_2$ dioxane with fresh $\{LO^3\}K$ with $KN(SiMe_3)_2$ brought no improvement. Similarly, $\{LO^3\}$ SnCl was obtained from SnCl₂ and $\{LO^3\}$ K but its reaction with $KN(SiMe_3)_2$ only led to partial formation of 7 (*ca.* 60%) together with unidentified species. Complexes 1–3, 5–10, $\{LO^3\}$ GeCl and $\{LO^3\}$ SnCl were isolated as analytically pure colourless solids. The plumbylene 11 could not be obtained entirely free of the homoleptic $\{LO^3\}_2Pb$ (a complex otherwise cleanly synthesized by reaction of $Pb(N(SiMe_3)_2)_2$ with 2 equiv of $\{LO^3\}H$). No reliable synthesis to the germylene 4 could be designed, as intractable mixtures were repeatedly recovered.²⁸ All complexes are soluble in aromatic hydrocarbons and ethers, and are sparingly so in petroleum ether; they are fully soluble in dichloromethane and do not react with this solvent through acid-base reaction.²⁹ All are stable in aromatic solvents as indicated by ¹H NMR monitoring, bar the kinetically labile **11** which rapidly evolves to generate $\{LO^3\}_2Pb$ and $Pb(N(SiMe_3)_2)_2$. The complexes were characterised by 1D and 2D solution NMR methods, including ${}^{29}Si{}^{1}H$ and, where relevant, ${}^{119}Sn{}^{1}H$ and 207 Pb{ 1 H} NMR spectroscopy. Except for **2**, **6** and **10** incorporating the simplest aminophenolate $\{LO^2\}^-$, the ¹H NMR spectra of all complexes in toluene- d_8 or benzene- d_6 showed high levels of fluxionality at 298 K, which hindered detailed assignment of the resonances for the side-arm hydrogens atoms; low temperature NMR in toluene- d_8 provided little help.

In the ¹H NMR spectra recorded in benzene- d_6 or toluene- d_8 at 298 K for the amido complexes **2**, **6**,^{14*a*} **10** and for {LO²}SnCl,^{14*a*} the two CH₂CH₃ groups onto the side-arm nitrogen atom are not equivalent. In **10** (Figure 1, top), the four N(CH₂CH₃)₂ methylene hydrogens are magnetically distinct, each being characterised by its own broad resonance (δ_{1H} **Dalton Transactions Accepted Manuscript**

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= 3.28, 2.84, 2.50 and 2.39 ppm), whereas two broad signals exchanging slowly at 298 Keventecle online found for the two N(CH₂CH₃)₂ methyl groups (centred on δ_{1H} = 0.74 and 0.57 ppm); this is indicative of overall C_1 symmetry, which was corroborated by crystallographic studies (*vide infra*). The fluxionality in **10** could be frozen at low temperature: sharp resonances were detected for all hydrogen atoms in the ¹H NMR spectrum recorded at 263 K (Figure 1, bottom), and they were readily assigned. At 368 K, the ArCH₂, NCH₂CH₃ and NCH₂CH₃ moieties in **10** each gives rise to a single resonance and the ¹H NMR spectrum agrees with *pseudo* C_s symmetry.

Fig. 1 ¹H NMR spectra (400.13 MHz, toluene- d_8) for {LO²}Pb(N(SiMe₃)₂) (**10**) recorded at 263 K (bottom) and 298 K (top). Solvent resonances are identified by *.

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Manual NMR line-shape analysis was performed for **10** in the temperature range $\frac{36624 \text{ tricle online}}{\text{boll: 16:1039/C3DT51681D}}$ 363 K, using a 0.1 M solution in toluene- d_8 . All changes observed in this range were reversible on return to 298 K. An overlay of the 0.30–1.80 ppm region of the ¹H NMR spectra (400.13 MHz) is displayed in Figure 2. Coalescence of the two resonances attributed to the two non-equivalent methyl groups in the N(CH₂CH₃)₂ moiety (two triplets centred on δ = 0.64 and 0.46 ppm in the slow regime at 263 K) was observed at T_c = 304 K.

Fig. 2 Stack of the 0.30–1.80 ppm region of the ¹H NMR spectra (400.13 MHz, toluene- d_8) of {LO²}Pb(N(SiMe₃)₂) (**10**) recorded in the temperature range 263–363 K.

Using $\delta v = 71$ Hz (determined at 263 K) leads to an estimate of $\Delta G^{\ddagger} = 14.6$ kcal·mol⁻¹ for the free energy of activation associated to the exchange between the ethyl groups. The

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corresponding enthalpy and entropy of activation $\Delta H^{\ddagger} = 14.8(0.5)$ kcal·mol⁻¹ and M^{\ddagger}_{DOI} Article online +0.7(1.6) cal·K⁻¹·mol⁻¹ were estimated by Eyring treatment of exchange rates determined by line-shape analysis (Figure 3). The variation of entropy associated to this process, which is assumed to proceed *via* dissociation-recoordination of the amino moiety, is surprisingly small. Arrhenius analysis led to $E_a = 15.5(0.5)$ kcal·mol⁻¹. The equation

$$E_{\rm a} = \Delta {\rm H}^{\ddagger} + m {\rm R} {\rm T} \tag{1}$$

where *m* is the order of the reaction corresponding to the fluxional changes, gives a kinetic order of 1 for this process for $T_c = 304$ K. A single resonance at *ca*. +2100 ppm is seen in the ²⁰⁷Pb{¹H} NMR spectra of **10** in this temperature range, which confirms the existence of a single environment.

Fig. 3 Eyring treatment of exchange rates determined by line-shape analysis (T = 263-363 K) for the dynamic behaviour of NCH₂CH₃ hydrogens in {LO²}Pb(N(SiMe₃)₂) (**10**).

Eyring and Arrhenius analysis were performed for $\{LO^2\}$ SnCl (in the range 298–368 K; $T_c = 322$ K), but treatment of the data for **2** (T = 233-363 K; $T_c = 318$ K) could not be

performed as relevant parameters (δv , $\Delta v_{\nu_2}^{e}$ and $\Delta v_{\nu_2}^{0}$, see the Supporting information) covint Article online not be determined accurately. Comparative data for **2**, **6**, **10** and {LO²} SnCl are collected in Table 1; they all are commensurate. Although performed over a limited temperature range, the data for {LO²} SnCl compare with those reported for **6**, confirming the reliability of the procedure. Identical phenomena, equivalent to a dynamic racemization process at a *pseudo*chiral 3-coordinate metal centre, must be at work in both cases.

Table 1. Summary of Eyring and Arrhenius analyses for fluxional processes in the $N(CH_2CH_3)_2$ fragments of 2, 6, 10 and $\{LO^2\}SnCl.^a$

Complex		T_c^{b}	δv^c	E_{a}	⊿G [‡]	${\it \Delta} { m H}^{\ddagger}$	${\it \Delta}{ m S}^{\ddagger}$
		(°C)	(Hz)	$(\text{kcal} \cdot \text{mol}^{-1})$	$(\text{kcal} \cdot \text{mol}^{-1})$	$(\text{kcal} \cdot \text{mol}^{-1})$	$(cal \cdot K^{-1} \cdot mol^{-1})$
${\rm LO}^{2}{\rm Ge}({\rm N}({\rm SiMe}_{3})_{2})$	(2)	318	n/a ^b	n/a ^b	+16.3	n/a ^b	n/a ^b
$\{LO^2\}$ Sn $(N(SiMe_3)_2)$	(6)	318	28	+13.6(0.3)	+16.0	+13.0(0.3)	-9.6(1.0)
LO^{2} Pb $(N(SiMe_{3})_{2})$	(10)	304	71	+15.5(0.5)	+14.6	+14.8(0.5)	+0.7(1.6)
{LO ² }SnCl		322	62	+13.2(0.1)	+16.4	+12.5(0.1)	-9.8(10.3)

^{*a*} NMR data recorded in toluene- d_8 ; data for **6** taken from reference 14*a*. ^{*b*} Coalescence temperature. ^{*c*} Difference of frequencies for the separated methyl groups at the lowest available temperature. ^{*b*} Could not be determined accurately.

Heteronuclear NMR data recorded at 298 K in aromatic solvents are collated in Table 2. The ²⁹Si{¹H} chemical shifts for **1–11** all fall in the same narrow range; the slight shift towards high fields on moving from germylenes to stannylenes and plumbylenes is consistent with increasing ionicity of the corresponding M–N_{amido} bond. The ¹¹⁹Sn{¹H} chemical shift (¹¹⁹Sn: $I = \frac{1}{2}$, natural abundance = 8.6%, receptivity relative to ¹H = 4.4 · 10⁻³) for the new stannylene **8** (–49.9 ppm) is nearly identical to those measured for **5–7**, and is diagnostic of a 3-coordinate, monomeric tin(II) centre.^{14a} Since ²⁰⁷Pb{¹H} chemical shifts for lead(II) compounds spread in the range –6000 to +3000 ppm (²⁰⁷Pb: $I = \frac{1}{2}$, natural abundance = 22.1%, receptivity relative to ¹H = 2.1 · 10⁻³), the similar resonances detected for the

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plumbylenes **9–11** (singlets between +2000 and +2150 ppm) testify to near-identical chevitic of the provided of the three metal centres. Since the aminophenolate ligand in **10** is devoid of side-arm oxygen atom, we concluded that the tethered O_{side-arm} atoms in **9** and **11** do not interact with the metal in solution. This postulate is in agreement with structural information obtained from XRD crystallography, and ²⁰⁷Pb{¹H} chemical shifts in the range +2000 to +2200 ppm are thus indicative of 3-coordinate, monomeric amino-phenolate lead(II) amides. By comparison, the homoleptic {LO³}₂Pb, featuring a 4-coordinate metal in the solid state (Supporting information), exhibits a shielded resonance at $\delta_{207Pb} = -367$ ppm.

Table 2. NMR data for 1–11, $\{LO^3\}_2Pb$, $\{LO^2\}SnCl$ and $\{LO^3\}SnCl$.^{*a*}

Complex		Solvent	²⁹ Si{ ¹ H}	$^{119}Sn{^{1}H}$	207 Pb{ 1 H}	Reference
			(ppm)	(ppm)	(ppm)	
${LO^1}Ge(N(SiMe_3)_2)$	(1)	toluene-d ₈	0.41	-	-	this work
${LO^2}Ge(N(SiMe_3)_2)$	(2)	toluene- d_8	0.06	-	-	this work
{LO ³ }Ge(N(SiMe ₃) ₂)	(3)	toluene- d_8	2.37	-	-	this work
${LO^1}Sn(N(SiMe_3)_2)$	(5)	toluene- d_8	-0.66	-63.8	-	14 <i>a</i>
${LO^2}Sn(N(SiMe_3)_2)$	(6)	benzene-d ₆	-0.63	-62.8	-	14 <i>a</i>
${LO^3}Sn(N(SiMe_3)_2)$	(7)	benzene-d ₆	-0.49	-55.0	-	6g
${LO^4}Sn(N(SiMe_3)_2)$	(8)	toluene- d_8	-0.34	-49.9	-	this work
{LO ² }SnCl		toluene- d_8	-	-218.1	-	14 <i>a</i>
{LO ³ }SnCl		toluene- d_8	-	-385.0	-	this work
${LO^1}Pb(N(SiMe_3)_2)$	(9)	toluene- d_8	-3.35	-	2007	this work
${LO^2}Pb(N(SiMe_3)_2)$	(10)	toluene- d_8	-2.35	-	2135	this work
${LO^3}Pb(N(SiMe_3)_2)$	(11)	benzene-d ₆	-3.29	-	2027	this work
$\{LO^3\}_2Pb$		benzene-d ₆	-	-	-367	this work

^a NMR data recorded at 25 °C.

The molecular structures of the germylenes 1-3 and $\{LO^3\}$ GeCl, stannylenes \S and $\{LO^3\}$ SnCl, and plumbylenes 9-11 were determined by X-ray diffraction measurements (Figures 4–12). Independently of the identity of the metal, all these complexes are monomeric in the solid state and feature 3-coordinate metal atoms. All amino(ether)-phenolate ligands lead to the formation of a 6-membered metallacycle through sole coordination of the O_{phenolate} and N_{side-arm} atoms as also observed for the amino-phenolate $\{LO^1\}^-$; where they could potentially occur, interactions between O_{side-arm} atoms and the metal were never detected. The environment about the metal is otherwise completed by Cl⁻ or the bulky amide N(SiMe₃)₂⁻. Pertinent metric parameters for these complexes as well as 5-7 are displayed in Table 3.

Fig. 4 ORTEP diagram of the molecular structure of $\{LO^1\}Ge(N(SiMe_3)_2)$ (1). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)-O(1) = 1.876(2), Ge(1)-N(1) = 1.901(2), Ge(1)-N(20) = 2.319(3); O(1)-Ge(1)-N(1) = 96.35(9), O(1)-Ge(1)-N(20) = 88.33(9), N(1)-Ge(1)-N(20) = 100.4(1).

Fig. 5 ORTEP diagram of the molecular structure of $\{LO^2\}Ge(N(SiMe_3)_2)$ (2). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)-O(1) = 1.872(1), Ge(1)-N(2) = 1.907(1), Ge(1)-N(27) = 2.294(1); O(1)-Ge(1)-N(2) = 94.52(6), O(1)-Ge(1)-N(27) = 90.22(6), N(2)-Ge(1)-N(27) = 100.60(6).

Fig. 6 ORTEP diagram of the molecular structure of $\{LO^3\}Ge(N(SiMe_3)_2)$ (**3**). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)-O(28) = 1.891(1), Ge(1)-N(21) = 1.913(1), Ge(1)-N(1) = 2.318(1); O(28)-Ge(1)-N(21) = 95.72(5), O(28)-Ge(1)-N(1) = 90.07(4), N(21)-Ge(1)-N(1) = 100.14(5).

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Fig. 7 ORTEP diagram of the molecular structure of $\{LO^3\}$ GeCl. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Only the main component of the disordered segment in the heterocycle side-arm (*viz* O9A) is represented. Selected bond lengths (Å) and angles (deg): Ge(1)–(O3)1 = 1.860(2), Ge(1)–N(15) = 2.189(2), Ge(1)–Cl(1) = 2.301(7); O(31)–Ge(1)–N(15) = 92.42(7), O(31)–Ge(1)–Cl(1) = 95.72(6), N(15)–Ge(1)–Cl(1) = 97.95(6).

Fig. 8 ORTEP diagram of the molecular structure of $\{LO^4\}Sn(N(SiMe_3)_2)$ (8). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)-O(1) = 2.064(1), Sn(1)-N(29) = 2.115(1), Sn(1)-N(17) = 2.419(1); O(1)-Sn(1)-N(29) = 93.78(5), O(1)-Sn(1)-N(17) = 86.55(4), N(29)-Sn(1)-N(17) = 95.62(5).

Fig. 9 ORTEP diagram of the molecular structure of $\{LO^3\}$ SnCl. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)–O(36) = 2.072(2), Sn(1)–N(1) = 2.357(2), Sn(1)–Cl(2) = 2.462(1); O(36)–Sn(1)–N(1) = 86.17(6), O(36)–Sn(1)–Cl(2) = 92.96(5), N(1)–Sn(1)–Cl(2) = 97.50(5).

Fig. 10 ORTEP diagram of the molecular structure of $\{LO^1\}Pb(N(SiMe_3)_2)$ (**9**). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pb(1)–O(1) = 2.220(4), Pb(1)–N(20) = 2.537(5), Pb(1)–N(31) = 2.243(5); O(1)–Pb(1)–N(31) = 93.7(2), O(1)–Pb(1)–N(20) = 83.9(2), N(31)–Pb(1)–N(20) = 95.8(2).

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Fig. 11 ORTEP diagram of the molecular structure of $\{LO^2\}Pb(N(SiMe_3)_2)$ (**10**). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pb(1)-O(1) = 2.186(2), Pb(1)-N(1) = 2.218(3), Pb(1)-N(20) = 2.536(3); O(1)-Pb(1)-N(1) = 92.61(9), O(1)-Pb(1)-N(20) = 83.97(9), N(1)-Pb(1)-N(20) = 97.9(1).

Fig. 12 ORTEP diagram of the molecular structure of $\{LO^3\}Pb(N(SiMe_3)_2)$ (**11**). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pb(1)-O(11) = 2.227(2), Pb(1)-N(1) = 2.237(2), Pb(1)-N(31) =

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2.543(2); O(11) - Pb(1) - N(1) = 91.51(8), O(11) - Pb(1) - N(31) = 84.68(8), N(1) - Pb(1) - NiewArticle Online DOI: 10.1039/C3DT51681D = 97.97(8).

Except for the M-heteroatom interatomic distances which increase regularly with the size of the metal (effective ionic radii for a coordination number of 6: Ge^{II}, 0.73 Å; Sn^{II}, unspecified; Pb^{II}, 1.19 Å; empirical atomic radius: Ge^{II}, 1.25 Å; Sn^{II}, 1.45 Å; Pb^{II}, 1.80 Å),³⁰ the geometric features of all complexes are very similar (Table 3). All heteroatom-metal-heteroatom angles are fairly close to 90 °. This suggests very limited or absence of hybridization between s and p valence orbitals, and, for a given metal, the character of the orbital for the lone pair of electrons is essentially ns^{2,31} All bond lengths fall in the expected range for such compounds. For a given ligand framework, there is no notable modification of the structural features for Ge/Sn/Pb complexes beyond the normal extension of the three M-heteroatom distances. For each family built on a same metal, bond distances and angles vary little between complexes with the exception of the N_{amine}-Sn-Cl angle for {LO³}SnCl (entry 10, 97.5 °) and {LO²}SnCl (entry 9, 89.5 °). This latter complex is rather peculiar, as the Namine-Sn-Cl angle is also much smaller than the corresponding Namine-Sn-N_{amine} angle found in the congeneric amido complex 6 (entry 6, 97.7 °), whereas no such discrepancy was found between the analogous pair of complexes $\{LO^3\}$ SnCl and 7. Comparison of entries 3 and 4 emphasizes that the nature of the X^{-} co-ligand, where X^{-} is either Cl⁻ or N(SiMe₃)₂⁻, should bear little influence of the geometric patterns around the metal.

Table 3. Relevant metric parameters for	or 1–3 , 5–11 ,	${LO^2}SnCl and$	$\{LO^3\}$ SnCl. ^{<i>a</i>}
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Entry	Complex		M-O _{phenolate}	М-Х	M-N _{amine}	Ophenolate-M-Namine	O _{phenolate} -M-X	N _{amine} -M-X	Reference
			(Å)	(Å)	(Å)	(deg)	(deg)	(deg)	
1	${LO^1}Ge(N(SiMe_3)_2)$	(1)	1.876(2)	1.901(2)	2.319(3)	88.33(9)	96.35(9)	100.4(1)	this work
2	${LO^2}Ge(N(SiMe_3)_2)$	(2)	1.872(1)	1.907(1)	2.294(1)	90.22(6)	94.52(6)	100.60(6)	this work
3	${LO^3}Ge(N(SiMe_3)_2)$	(3)	1.891(1)	1.913(1)	2.318(1)	90.07(4)	95.72(5)	100.14(5)	this work
4	{LO ³ }GeCl		1.860(2)	2.301(7)	2.189(2)	92.42(7)	95.72(6)	97.95(6)	this work
5	${LO^1}Sn(N(SiMe_3)_2)$	(5)	2.077(1)	2.128(2)	2.469(2)	85.43(5)	91.24(5)	95.95(6)	14 <i>a</i>
6	${LO^2}Sn(N(SiMe_3)_2)$	(6)	2.066(3)	2.102(4)	2.435(3)	86.6(1)	94.0(1)	97.7(1)	14 <i>a</i>
7	${LO^3}Sn(N(SiMe_3)_2)$	(7)	2.074(1)	2.112(1)	2.437(1)	86.08(4)	94.06(4)	96.78(4)	6g
8	${LO^4}Sn(N(SiMe_3)_2)$	(8)	2.064(1)	2.115(1)	2.419(1)	86.55(4)	93.78(5)	95.62(5)	this work
9	{LO ² }SnCl		2.036(2)	2.506(7)	2.393(2)	86.18(7)	93.79(6)	89.46(5)	14 <i>a</i>
10	{LO ³ }SnCl		2.072(2)	2.468(1)	2.357(2)	86.17(6)	92.96(5)	97.50(5)	this work
11	${LO^1}Pb(N(SiMe_3)_2)$	(9)	2.220(4)	2.243(5)	2.537(5)	83.9(2)	93.7(2)	95.8(2)	this work
12	$\{LO^2\}Pb(N(SiMe_3)_2)$	(10)	2.186(2)	2.218(3)	2.536(3)	83.97(9)	92.61(9)	97.9(1)	this work
13	${LO^3}Pb(N(SiMe_3)_2)$	(11)	2.227(2)	2.237(2)	2.543(2)	84.68(8)	91.51(8)	97.97(8)	this work
^{a} M = C	^{<i>a</i>} $M = Ge^{II}$, Sn^{II} or Pb^{II} ; $X = Cl$ or $N(SiMe_3)_2$								

The structural features of family $\{LO^3\}M(N(SiMe_3)_2 (M = Ge, 3; Sn, 7; Pb, 11))$ where the amino(ether)-phenolate incorporates the aza-15-crown-5 tether are of particular interest. Because none of the O_{side-arm} atoms is coordinated onto the metal, we postulated they could be employed for further coordination chemistry involving an additional metallic centre. The high affinity of (aza-)crown ethers for cationic metals has been demonstrated, and can be exploited to design ion sensors acting through selective ligation of metal ions.³² Macrocycles containing 5 heteroatoms such as 15-crown-5 and 1-aza-15-crown-5 are ideally suited to the binding of the small Li⁺ and Na⁺ alkali ions,^{32b} and we reasoned that salts of these metals could be combined with 3, 7 and/or 11 to prepare heterobimetallic complexes through inclusion of the hard cation in the anchored macrocycle of the $\{LO^3\}^-$ ligand. A related approach was implemented by Jurkschat and co-workers, who provided elegant spectroscopic evidence for the formation of tin(IV)-halide bimetallic species upon addition of various alkali halides to solutions of their bis(crown ether)-substituted organostannanes X₂Sn(CH₂-[16]-crown-₅)₂ (X = Br, I).³³ Also, Batten and co-workers have just reported manganese- or cuprous-potassium heterobimetallic coordination polymers using a functionalised diaza-18-crown-6 ligand possessing pendant *p*-pyridylpyrazole side-arms.³⁴

In a preliminary reaction, the proteo-ligand $\{LO^3\}H$ (a colourless oil)³⁵ was reacted with LiOTf in diethyl ether (Scheme 2). The ¹H and ¹³C{¹H} NMR data for the white solid ($\{LO^3\}H\cdot LiOTf$) obtained quantitatively after evaporation was different from those for $\{LO^3\}H$, suggesting that the lithium cation was ligated by the macrocyclic heteroatoms. This was confirmed by X-ray diffraction crystallography, which shows the alkali metal to sit in the pocket formed by the four O_{side-arm} atoms and to be further coordinated by one oxygen atom from the triflate counter-ion, whereas the N_{side-arm} atom is not involved in the coordination sphere of the metal (Figure 13). The geometry about the metal constitutes a distorted square Transactions Accepted Manuscript

pyramidal ($\tau = 0.36$),³⁶ with the tightly bound O_{triflate} atom occupying the apical position View Article Online the O_{side-arm} atoms being more remote from the metal.

Scheme 2. Synthesis of heterobimetallic compounds

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As the molecular structures of **3** and $\{LO^3\}H\cdot LiOTf$ offered the structural features required to the formation of an heterobimetallic complex, the reaction of the latter with $Ge(N(SiMe_3)_2)_2$ was attempted, but it failed to yield the mixed Ge^{II} -Li species (Scheme 2). Instead, the desired complex **3**·LiOTf was obtained by equimolar reaction between the

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germylene **3** and lithium triflate. It is a colourless solid soluble in ethers and aromatic. View Article Online hydrocarbons, but insoluble in light petroleum. It was characterised by NMR spectroscopy and X-ray diffraction crystallography, but the presence of residual {LO³}H·LiOTf could not be avoided, which precluded good combustion analysis.

Fig. 13 ORTEP diagram of the molecular structure of $\{LO^3\}H\cdot LiOTf$. Ellipsoids drawn at the 50% probability level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Li(1)–O(103) = 1.940(5), Li(1)–O(10) = 2.105(5), Li(1)–O(7) = 2.105(5), Li(1)–O(13) = 2.138(5), Li(1)–O(4) = 2.159(5); O(103)–Li(1)–O(10) = 119.5(3), O(103)–Li(1)–O(7) = 100.3(2), O(10)–Li(1)–O(7) = 77.86(18), O(103)–Li(1)–O(13) = 105.5(2), O(10)–Li(1)–O(13) = 77.46(19), O(7)–Li(1)–O(13) = 150.7(3), O(103)–Li(1)–O(4) = 109.5(3), O(10)–Li(1)–O(4) = 128.9(2), O(7)–Li(1)–O(4) = 80.27(18), O(13)–Li(1)–O(4) = 103.5(2).

The molecular solid state structure of **3**·LiOTf is remarkable (Figure 14). It can be divided into two fragments which virtually do not interact with each other: one pertaining to the amino-phenolate Ge(II) amide, and the other relating to the a polyether-LiOTf moiety. The triflate anion tightly bound to the Li atom and the bulky amido group $N(SiMe_3)_2^-$ are

located in *trans* position with respect to the plane defined by the five heteroatoms of the View Article Online macrocycle, so that they impart minimal steric congestion to the coordination spheres of either of the two metals. All bonding patterns and metric parameters for the 3-coordinate Ge^{II} centre in **3·LiOTf** match closely those described for **3** alone, whereas those measured around the 5-coordinate Li centre ($\tau = 0.33$)³⁶ are very similar to those found for {LO³}H·LiOTf. The large Ge^{II}...Li distance (5.85 Å) rules out the existence of metallophilic interactions.

Fig. 14 ORTEP diagram of the molecular structure of **3**·**LiOTf**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)-O(11) = 1.871(1), Ge(1)-N(1) = 1.902(1), Ge(1)-N(31) = 2.335(1), O(34)-Li(51) = 2.081(3), O(37)-Li(51) = 2.096(3), O(40)-Li(51) = 2.034(3), O(43)-Li(51) = 2.081(3), Li(51)-O(52) = 1.885(3); O(11)-Ge(1)-N(1) = 96.23(6), O(11)-Ge(1)-N(31) = 89.49(5), N(1)-Ge(1)-N(31) = 99.04(6), O(52)-Li(51)-O(40) = 117.82(16), O(52)-Li(51)-O(43) = 105.45(15), O(40)-Li(51)-O(43) = 78.32(12), O(52)-Li(51)-O(34) = 111.26(16), O(40)-Li(51)-O(34) = 130.15(16), O(43)-Li(51)-O(34) = 97.17(14), O(52)-Li(51)-O(37) = 102.34(16), O(40)-Li(51)-O(37) = 78.46(12), O(43)-Li(51)-O(37) = 149.81(17), O(34)-Li(51)-O(37) = 83.41(12).

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The heterobimetallic Sn^{II} -Li complex **7**·LiOTf was also prepared by reaction of **7**^{iext} dicte online boil 18.1039/C3DT51681D lithium triflate, since the reaction of $\{LO^3\}H\cdot LiOTf$ and $Sn(N(SiMe_3)_2)_2$ proved unsuccessful (Scheme 2). The solid state structure of the Sn^{II} -Li bimetallic complex **7**·LiOTf is depicted in Figure 15. All attempts to obtain the lead(II) analogue of **3**·LiOTf and **7**·LiOTf failed: the kinetic lability of **11** and its contamination by $\{LO^3\}_2Pb$ (*vide supra*) preclude its use as an efficient precursor, while no reaction took place between $\{LO^3\}H\cdot LiOTf$ and $Pb(N(SiMe_3)_2)_2$.

Fig. 15 ORTEP diagram of the molecular structure of **7**·**LiOTf**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)-O(31) = 2.0880(15), Sn(1)-N(32) = 2.1137(17), Sn(1)-N(15) = 2.4860(17), Li-O(45) = 1.893(4), Li-O(6) = 2.025(4), Li-O(12) = 2.040(4), Li-O(9) = 2.111(4), Li-O(3) = 2.142(4); O(31)-Sn(1)-N(32) = 96.86(6), O(31)-Sn(1)-N(15) = 84.41(6), N(32)-Sn(1)-N(15) = 99.47(6), O(45)-Li-O(6) = 105.55(19), O(45)-Li-O(12) = 117.6(2), O(6)-Li-O(12) = 136.29(19), O(45)-Li-O(9) = 107.82(19), O(6)-Li-O(9) = 79.19(15), O(12)-Li-O(9) = 81.14(15), O(45)-Li-O(3) = 100.42(18), O(6)-Li-O(3) = 81.44(15), O(12)-Li-O(3) = 96.91(17), O(9)-Li-O(3) = 149.11(19).

The molecular structure of **7**·**LiOTf** resembles closely that of **3**·**LiOTf**, with a 3-view Article Online coordinate tin(II) centre and a 5-coordinate lithium atom in a square pyramidal environment $(\tau = 0.21)$.³⁶ The geometries and interatomic distances around the Sn^{II} and Li atoms in **7**·**LiOTf** match those found in the parent compounds **7** and {LO³}H·LiOTf, even if Li–O_{side}arm and Li–O_{triflate} bond lengths in this latter compound are a little longer than in the heterobimetallic complex. There is no Sn^{II}…Li interaction on account of the long intermetallic distance (6.06 Å).

On the whole, in the solid state, the inclusion of the small alkali metal bears no impact on the coordination sphere about the *p*-block metal in these amino(crown-ether)-phenolate complexes, be it with germanium(II) or the larger tin(II). This is also likely so in solution, as indicated by heteronuclear NMR spectroscopy.³⁷ The ¹¹⁹Sn{¹H} data recorded for **7** and **7·LiOTf** ($\delta_{sn} = -55.0$ and -45.8 ppm, respectively) in dichloromethane- d_2 (owing to limited solubility of the latter in aromatic hydrocarbons) are nearly identical; the corresponding ²⁹Si{¹H} chemical shifts are also very similar ($\delta_{si} = -0.75$ and -0.31 ppm), and the ⁷Li{¹H} chemical shift for **7·LiOTf** ($\delta_{Li} = -0.56$ ppm) matched that for the tin-free {LO³}H·LiOTf ($\delta_{Li} = -0.84$ ppm) in this solvent. Moreover, in benzene- d_6 or toluene- d_8 , the ⁷Li{¹H} ($\delta_{Li} =$ -0.74 ppm) and ²⁹Si{¹H} ($\delta_{Si} = +0.70$ ppm) resonances for **3·LiOTf** are comparable to those for {LO³}H·LiOTf ($\delta_{Li} = -0.96$ ppm) and **3** ($\delta_{Si} = 2.37$ ppm), respectively.

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Although the size of the macrocyclic side-arm is in principle suited to the binding of sodium ions,³² attempts to such insertions using sodium triflate or the $[Na(OEt_2)_4]^+ \cdot [H_2N\{B(C_6F_5)_3\}_2]^-$ loose ion pair,³⁸ failed to deliver heterobimetallic complexes with either **3** or **7**. Efforts to prepare bimetallic species starting from complex **8** where the macrocycle contains only four heteroatoms also met no success, although NMR data showed that $\{LO^4\}H\cdot LiOTf$ could be synthesised. The ability of the highly chelating $\{LO^3\}^-$ to yield polymetallic alkali species had previously been highlighted through ready formation of

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 ${LO^3}Li \cdot LiN(SiMe_2H)_2^{13i}$ and $[{LO^3}K \cdot KN(SiMe_2H)_2]_1^{13d}$ although the challenges overview detice online for the preparation of **3**·LiOTf and **7**·LiOTf were greater than those associated to these homobimetallic alkali complexes. We have in the past failed to prepare the Zn–Li equivalent to **3**·LiOTf and **7**·LiOTf, perhaps because the ionic nature of the Zn–O and Li–O bonds led to deleterious redistribution reactions. The ability of the tethered side-arm in ${LO^3}^-$ to perfectly host Li⁺ salts also precludes the use of ${LO^3}Li$ species for salt metathesis reactions; as intractable mixtures are always obtained from such reactions; this is why ${LO^3}K$ was used instead to obtain ${LO^3}GeCl$ and ${LO^3}SnCl$ (*vide supra*).

Ring-opening polymerisation studies

The performance of complexes **1**–**3** and **5**–**10** in the catalysis of the immortal ring-opening polymerisation (*i*ROP) of L-lactide (L-LA) or racemic-lactide (*rac*-LA) upon addition of *i*PrOH was probed (Scheme 3).^{2c,39} The heterobimetallic **3·LiOTf** and **7·LiOTf** were also assessed to gauge the influence of the additional alkali metal, but the heteroleptic chloro derivatives were not interrogated because (*i*) their behaviour in the presence of (excess) alcohol is often erratic, and (*ii*) chloride is a very poor initiating group. Complex **11**, which could not be obtained free of impurity, was also excluded from this screening. Reactions were typically performed in toluene at 60–100 °C, using 500–1,000 equiv of lactide and 10–25 equiv of alcohol *vs.* metal, and [lactide]₀ = 2.0 M.

Scheme 3

Entry	Precat.	LA	[LA] ₀ /[Precat] ₀ /[<i>i</i> PrOH] ₀	T ^{re}	time	Yield ^b	$M_{\rm n,theo}^{\ \ c}$	$M_{n,SEC}^{d}$	$M_{ m w}/M_{ m n}{}^d$	$M_{n,NMR}^{e}$	$P_{\rm r}^{f}$
				(°C)	(min)	(%)	$(g \cdot mol^{-1})$	$(g \cdot mol^{-1})$		$(g \cdot mol^{-1})$	
1	1	L-	500:1:10	100	360	74	5,400	7,100	1.21	4,800	
2	2	L-	500:1:10	100	360	82	6,000	8,100	1.13	5,200	
3	3	L-	500:1:10	100	360	35	2,600	3,600	1.09	2,900	
4	3	L-	1,000:1:10	100	360	15	2,200	2,900	1.07	2,700	
5	3·LiOTf	L-	500:1:10	100	360	57	4,100	5,600	1.06	4,800	
6	3·LiOTf	L-	1,000:1:10	100	360	34	5,000	5,600	1.06	4,000	
7	5	L-	1,000:1:10	60	180	88	12,700	12,900	1.07	11,700	
8	6	L-	1,000:1:10	60	180	88	12,700	13,300	1.06	9,100	
9 ^{<i>g</i>}	7	L-	1,000:1:10	60	180	87	12,500	11,900	1.11	13,600	
10	8	L-	1,000:1:10	60	180	95	13,800	14,800	1.06	9,700	
11	7·LiOTf	L-	1,000:1:10	60	180	22	3,200	4,500	1.08	2,000	
12	9	L-	1,000:1:10	60	3	92	13,300	14,000	1.09	12,400	
13	9	L-	1,000:1:10	60	12	93	13,400	13,200	1.21	12,500	
14	9	L-	1,000:1:10	60	60	92	13,300	15,000	1.30	13,800	
15 ^{<i>h</i>}	9	L-	5,000:1:25	60	45	96	27,700	26,200	1.10	26,000	
16	9	L-	500:1:10	100	180	87	6,300	11,500	1.44	6,500	
17	10	L-	500:1:10	100	180	87	6,300	9,900	1.43	5,600	
18	2	rac-	500:1:10	100	360	66	4,800	7,000	1.15	4,500	0.68
19 ^g	7	rac-	1,000:1:10	60	180	92	13,300	10,300	1.13	8,200	0.61
20	9	rac-	1,000:1:10	60	12	92	13,300	9,200	1.23	13,800	0.48

Table 4. *i*ROP of lactide promoted by 1–3, 5–10, 3·LiOTf or 7·LiOTf in association with *i*PrOH.^{*a*}

^{*a*} Polymerisations in toluene, $[lactide]_0 = 2.0$ M unless otherwise stated. ^{*b*} Isolated yield of PLA after precipitation. ^{*c*} $M_{n,theo} = [lactide]_0/[iPrOH]_0 \times yield \times 144.13 + M_{iPrOH}$. ^{*d*} Determined by SEC *vs*. polystyrene standards, and corrected by a factor of 0.58.⁴⁰ ^{*e*} Determined by end-group analysis. ^{*f*} Determined by homodecoupled ¹H NMR spectroscopy. ^{*g*} From reference 6g. ^{*h*} [L-lactide]_0 = 4.0 M.

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Several trends emerge rapidly from examination of the data collected in Table 4. View Article Online DOI: 10.1039/C3DT51681D combination with iPrOH (10 equiv), which acts both as a co-catalyst and a chain transfer agent, all tested complexes afford binary catalytic systems for ROP reactions presenting a high level of control over the macromolecular features (qualitatively measured by the good agreement between theoretical and experimentally determined (by SEC or NMR) molecular weights, and by the narrow polydispersity index M_w/M_p). Yet, the activity changes drastically with the size of the metal, as reaction rates increase with metal size according to $Ge^{II} \ll Sn^{II}$ << Pb^{II}. Where germylenes require 6 h to convert only partly 500 equiv of monomer at 100 °C (entries 1-3), nearly full conversion is achieved within 3 h at 60 °C with the stannylenes (entries 7–10) while the plumbylene 9 fully converts 1,000 equiv of monomer in as little as 3 min at 60 °C (entry 12). Increase of ROP catalytic activity with metal size has already been reported for alkaline-earth metals,^{6j,6l,41} but this cannot be extended to all groups has for instance such relationship cannot be drawn for metals of groups 4 and 13.^{2a,2g-h} In this series of compounds, for a given metal, the identity of the ligand bears limited influence, if any, on the final outcome of the polymerisation; compare for instance entries 1-3, 5-8 and 16-17, an observation which has already been discussed elsewhere in details in the case of tin(II) precatalysts.^{6g} The polymerisation of *rac*-lactide proceeds with rates and control comparable to those of L-lactide, but the resulting polymers are essentially atactic (entries 18–20). Endgroup analysis (NMR and MALDI-ToF MS) confirmed the identity of the expected termini $(-CH(CH_3)OH \text{ and } (CH_3)_2CHOC(=O)-).$

Although they afford excellent control over the reactions parameters, the germylenes 1-3 are crippled by excessively low reaction rates, which in practise rules out their use as good ROP precatalysts, at least for the polymerisation of lactide. The presence of LiOTf had a beneficial effect on the catalytic activity of the germylene **3**, as **3**·LiOTf proved substantially more active under otherwise identical experimental conditions (entries 3 *vs.* 5 and 4 *vs.* 6).

Although the nature of the ROP mechanism mediated by $3 \cdot \text{LiOTf}/i\text{PrOH}$ has not been view Article Online elucidated, a possible intuitive explanation can be proposed: one may envisage that the strong Lewis acid Li⁺ (although tamed by coordination of the crown ether) acts as an activator for the incoming monomer in a way reminiscent of the so-called "activated monomer" ^{2c} or "dualcatalyst"⁴² ROP mechanisms. The fact that, by contrast, $7 \cdot \text{LiOTf}$ afforded lower conversion than 7 (entries 9 and 11) probably arises from the much greater sensitivity of the former compared to $3 \cdot \text{LiOTf}$, which may result in rapid catalyst decomposition under catalytic conditions. The catalytic performances of 5-7 (that of 8 is strictly analogous) have already been discussed elsewhere and will not be further detailed here.^{6g}

The lead-based binary system **9**/*i*PrOH proved most effective. Under controlled conditions, it afforded very rapidly narrowly dispersed polymers of predictable lengths (entries 12, 15 and 20). Large quantities of monomer (5,000 equiv *vs.* Pb^{II}) were fully converted into medium molecular weight material within 45 min under mild conditions, and the resulting material exhibits excellent control over the molecular masses. In terms of combined productivity and activity, this stands on equal foot with performances achieved with highly effective zinc-based systems for the polymerisation of lactide.^{13*b*,13*e*} The rapid increase in polydispersity observed after full conversion, which results from deleterious transesterification reactions, further testifies to the high reactivity of the binary catalyst **9**/*i*PrOH (entries 12–14). The utilisation of the other plumbylene, **10**, was not investigated in details, but based on the limited role of the ligand under the chosen experimental conditions (*vide supra*), similar result may be anticipated.

Conclusion

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Complete families of stable monomeric germylenes, stannylenes and plumbylenes supported by multidentate amino-, amino(ether)- and amino(crown-ether)-phenolate ligands are now

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available. The combination of crystallographic and heteronuclear NMR studies shows that we article online independently of the nature of the metal centre and that of the co-ligand, the metal centre systematically exists in a 3-coordinate environment. Therefore, from a strict coordination point-of-view, the simple amino-phenolate $\{LO^2\}^-$ is as good a ligand as the more encumbered and electron-donating amino(ether)- and amino(crown-ether)-phenolates $\{LO^1\}^$ and $\{LO^3\}^-$, respectively. The NMR signature of these complexes containing NMR-active metal centres is readily provided by ¹¹⁹Sn{¹H} and ²⁰⁷Pb{¹H} NMR spectroscopies.

The fact that the metal in these divalent group 14 metallenes is satisfied in a 3coordinate coordination environment enables the preparation of heterobimetallic complexes by inclusion of lithium salts in the crown-ether side-arm of the ligand $\{LO^3\}^-$, at least with germanium(II) and tin(II) for which the metal– $O_{phenolate}$ bond is fairly covalent. So far only LiOTf has been used for this purpose with success, but several other complexes could in principle be obtained upon expanding the size of the crown-ether, and future efforts could aim at chelating a variety of monocations of alkali, coinage or triel metals.

If the catalytic activity of the simple germylenes, and in particular that supported by the amino-crown ether-phenolate {LO³}⁻, for the polymerisation of lactide was disappointing, preliminary results suggest it may be possible to boost their performance by inclusion of judicious cations in the macrocyclic tether. On the other hand, the plumbylenes have revealed excellent ability for the ROP of L-lactide, both in terms on control and reaction rates. Of course, the toxicity of lead is a major liability that under normal circumstances would immediately rule it out as a potential candidate for catalyst development in this field. However, maximising reaction rates and monomer loadings to the point where only ppm levels of metal catalyst are required should alleviate partly this issue, and in this aim we are now trying to develop other lead(II) precatalysts for immortal ROP catalysis.

Experimental section

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General procedures. All manipulations were performed under inert atmosphere using standard Schlenk techniques or in a dry, solvent-free glove-box (Jacomex; $O_2 < 1$ ppm, $H_2O <$ 5 ppm) for catalyst loading. SnCl₂ (Acros, 98%), PbCl₂ (Strem), GeCl₂ dioxane (Acros) and LiOTf (Strem) were used as received. HN(SiMe₃)₂ (Acros) was dried over activated molecular sieves and distilled prior to use. Benzyl alcohol was dried and distilled over magnesium turnings and stored over 3 Å molecular sieves. Potassium tert-butoxide was freshly (190 °C under dynamic vacuum $< 10^{-2}$ Torr) sublimed prior to use. Ge(N(SiMe₃)₂)₂,⁴³ $Sn(N(SiMe_3)_2)_2$,⁴⁴ (Pb(N(SiMe_3)_2)_2),⁴³ {LO¹} Sn(N(SiMe_3)_2) (6),^{14a} {LO²} Sn(N(SiMe_3)_2) (7),^{14*a*} {LO³}Sn(N(SiMe_3)₂) (8),^{6g} {LO³}K,^{13*h*} and the pro-ligands {LO¹}H-{LO⁴}H^{35,45} were prepared following literature protocols. Solvents (THF, Et₂O, CH₂Cl₂, pentane and toluene) were purified and dried (water contents below 8 ppm) over columns alumina (MBraun SPS). THF was further distilled under argon from sodium mirror/benzophenone ketyl. 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-vacuum cycles. Technical grade L-LA was provided by Total Petrochemicals and purified by recrystallization from a hot (80 °C), concentrated *i*PrOH solution, followed by two subsequent recrystallizations in hot (105 °C) toluene. After purification, L-lactide was stored at all times at a temperature of -30 °C in the inert atmosphere of the glove-box. Racemic lactide (Acros) was purified in the same way.

NMR spectra were recorded on Bruker AC-300, AM-400 and AM-500 spectrometers. All ¹H and ¹³C{¹H} chemicals shifts were determined using residual signals of the deuterated solvents and were calibrated *vs*. SiMe₄. Assignment of the signals was carried out using 1D (¹H, ¹³C{¹H}) and 2D (COSY, HMBC, HMQC) NMR experiments. ¹⁹F{¹H} chemical shifts were determined by external reference to an aqueous solution of NaBF₄. A capillary

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containing an aqueous solution of LiCl ($\delta_{7\text{Li}} = 0$ ppm) was used for the calibration of ⁷L₁ View Article Online NMR spectra. ²⁰⁷Pb NMR spectra were referenced against a solution of Pb[N(SiMe_3)_2]_2 in benzene- d_6 ($\delta_{207\text{Pb}} = +4916$ ppm). ¹¹⁹Sn NMR spectra were externally calibrated vs. SnMe₄.

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

Size Exclusion Chromatography (SEC) measurements were performed on an Agilent PL-GPC50 equipped with two PLgel 5Å MIXED-C columns and a refractive index detector. The column was eluted with THF at room temperature at 1.0 mL \cdot min⁻¹ and was calibrated using 11 monodisperse polystyrene standards in the range of 580 to 380,000 g \cdot mol⁻¹. The molecular weights of all PLAs were corrected by a factor of 0.58.⁴⁰

[LO¹]Ge(N(SiMe₃)₂) (1). A solution of {LO¹}H (0.35 g, 1.00 mmol) in diethyl ether (20 mL) was added at -30 °C over a period of 30 min to a solution of Ge(N(SiMe₃)₂)₂ (0.40 g, 1.02 mmol) in diethyl ether (20 mL). The colour of the solution gradually discharged from deep orange to light yellow. The resulting mixture was warmed to room temperature and stirred overnight, and the volatiles were removed under vacuum. The resulting powder was washed with cold pentane (2 mL) at -20 °C and dried *in vacuo* to give pure **1** as a colourless powder (0.51 g, 87%). Single-crystals of **1** suitable for X-ray diffraction crystallography were obtained by recrystallisation from a cold mixture of pentane and toluene. ¹H NMR (toluene-*d*₈, 500.13 MHz, 0 °C): *δ* = 7.60 (d, ⁴*J*_{HH} = 2.5 Hz, 1H, aromatic-*H*), 7.00 (d, ⁴*J*_{HH} = 2.5 Hz, 1H, aromatic-*H*), 3.53–3.46 (m, 2H, CH(*H*)OCH₃ and ArC*H*(H)N), 3.43–3.38 (m, 1H, CH(*H*)OCH₃), 3.23–3.20 (m, 1H, NC*H*₂CH₂), 3.09 (s, 3H, OC*H*₃), 2.97–2.91 (m, 4H, NC*H*₂CH₂ and OC*H*₃), 2.89–2.82 (m, 1H, NC*H*₂CH₂), 2.81–2.74 (m, 1H, NC*H*₂CH₂), 1.70 (s,

9H, C(CH₃)₃), 1.39 (s, 9H, C(CH₃)₃), 0.59 (s, 9 H, (Si(CH₃)₃)₂), 0.46 (s, 9 H, (Si(CH₃)₃)₂), View Article online ppm. ¹³C{¹H} NMR (toluene- d_8 , 125.62 MHz, 0 °C): δ = 156.15, 140.65, 140.61, 126.05, 125.56 and 124.30 (all aromatic-C), 68.99 and 66.93 (both OCH₂), 58.18 and 58.07 (both OCH₃), 57.74 (ArCH₂N), 52.71 and 51.48 (both NCH₂CH₂), 34.83 (*C*(CH₃)₃), 34.06 (*C*(CH₃)₃), 31.64 (C(CH₃)₃), 30.33 (C(CH₃)₃), 6.61 and 5.41 (both N(Si(CH₃)₃)₂) ppm. ²⁹Si{¹H} NMR (toluene- d_8 , 79.49 MHz, 25 °C): δ = 0.41 ppm. Elemental analysis for C₂₇H₅₄GeN₂O₃Si₂ (583.54 g·mol⁻¹): theoretical, C 55.6%, H 9.3%, N 4.8%; found C 55.7%, H 10.0%, N 4.7%.

{LO²}Ge(N(SiMe₃)₂) (2). Following a protocol similar to that described for **1**, the reaction of $\{LO^2\}H$ (0.29 g, 1.00 mmol) and Ge(N(SiMe₃)₂)₂ (0.40 g, 1.02 mmol) afforded **2** as a white powder (0.31 g, 47%). Single-crystals of **2** suitable for X-ray diffraction studies were grown from a cold mixture of pentane and toluene.¹H NMR (toluene-*d*₈, 500.13 MHz, 25 °C): *δ* = 7.54 (d, ⁴*J*_{HH} = 2.5 Hz, 1H, aromatic-*H*), 6.85 (d, ⁴*J*_{HH} = 2.5 Hz, 1H, aromatic-*H*), 3.77 (AB spin,²*J*_{HH}= 13.6 Hz, 1H, ArCH(*H*)N), 2.92 (AB spin,²*J*_{HH}= 13.6 Hz, 1H, ArCH(H)N), 2.83− 2.04 (br m, 4H, NCH₂CH₃), 1.63 (s, 9H, C(CH₃)₃), 1.36 (s, 9H, C(CH₃)₃), 0.73−0.68 (br m, 6H, ³*J*_{HH} = 7.5 Hz, both NCH₂CH₃), 0.48− 0.38 (br m, 18H, N(Si(CH₃)₃)) ppm. ¹³C {¹H} NMR (toluene-*d*₈, 125.62 MHz, 25 °C): *δ* = 156.70, 141.26, 141.07, 125.98, 125.43 and 124.82 (all aromatic-*C*), 56.40 (ArCH₂N), 45.79 and 45.33 (both NCH₂CH₃), 35.38 (C(CH₃)₃), 34.59 (C(CH₃)₃), 32.20 (C(CH₃)₃), 30.93 (C(CH₃)₃), 9.27 and 7.04 (both NCH₂CH₃), 7.18 and 6.07 (both N(Si(CH₃)₃)₂) ppm. ²⁹Si{¹H} NMR (toluene-*d*₈, 79.49 MHz, 25 °C): *δ* = 0.06 ppm. Elemental analysis for C₂₅H₅₀GeN₂OSi₂ (523.49 g·mol⁻¹): theoretical, C 57.4%, H 9.6%, N 5.3%; found C 57.2%, H 9.7%, N 5.4%.

 $\{LO^3\}Ge(N(SiMe_3)_2)$ (3). *Method 1*: K(N(SiMe_3)_2) (0.40 g, 2.00 mmol) was added in <u>View Article online</u> portions with a bent finger to a solution of $\{LO^3\}H$ (0.44 g, 1.00 mmol) in THF (15 mL). After stirring for 2 h at room temperature, the resulting solution was added dropwise to a solution of GeCl₂·dioxane in THF. The reaction mixture was stirred overnight. After removing the volatiles under reduced pressure, the crude product was extracted with pentane (3 × 10 mL). The solution was then taken to dryness and the resulting foam was stripped with pentane (4 × 3 mL). The resulting pale yellow solid was washed with pentane (4 mL) and dried *in vacuo* to constant weight to give **3** as white powder (0.31 g, 46%). *Method 2*: A solution of $\{LO^3\}H$ (0.44 g, 1.00 mmol) in diethyl ether (20 mL) was added at

-30 °C over a period of 30 min to a solution of Ge(N(SiMe_3)_2)_2 (0.40 g, 1.02mmol) in diethyl ether (20 mL). A rapid change of coloration from deep orange to light yellow was observed. The resulting mixture was warmed to room temperature and stirred overnight, and the volatiles were removed under vacuum. The resulting powder was washed with cold pentane (3 mL) at -20 °C and dried *in vacuo* to give analytically pure **3** as a white powder (0.54 g, 81 %).

Single-crystals of **3** suitable for X-ray diffraction crystallography were obtained by recrystallisation from pentane. ¹H NMR (toluene- d_8 , 400.13 MHz, 25 °C): $\delta = 7.61$ (d,⁴ $J_{HH} =$ 2.5 Hz, 1H, aromatic–H), 6.99 (d,⁴ $J_{HH} = 2.5$ Hz, 1H, aromatic–H), 4.02 (AB spin,² $J_{HH} = 13.6$ Hz, 1H, ArCH(H)N), 3.84–3.79 (br m, 3H, OC H_2CH_2O), 3.47 (AB spin,² $J_{HH} = 13.6$ Hz, 1H, ArCH(H)N), 3.46–3.23, 3.17–3.13 and 2.85–2.72 (br m, 17H, OC H_2CH_2O and NC H_2CH_2), 1.65(s, 9H, C(C H_3)₃), 1.36 (s, 9H, C(C H_3)₃), 0.52(br, 9H, N(Si(C H_3)₃)₂), 0.43 (br, 9H, N(Si(C H_3)₃)₂) ppm. ¹³C{¹H} NMR (benzene- d_6 , 100.62 MHz, 25 °C): $\delta = 156.71$, 141.11, 141.08, 126.53, 125.89 and 124.63 (all aromatic-C), 71.77, 71.30, 70.73, 70.57, 70.50, 67.39 and 65.96 (all OCH₂), 56.77 (ArC H_2 N), 53.69 and 52.84 (NCH₂CH₂O), 35.21 and 34.42 (both C(CH₃)₃), 32.03 and 30.79 (both C(CH_3)₃), 6.93 and 5.90 (both (Si(CH_3)₃)₂) ppm. ²⁹Si{¹H} Transactions Accepted Manuscript

NMR (benzene- d_6 , 79.49 MHz, 25 °C): $\delta = 2.37$ ppm. Elemental analysis for View Article Online DOI: 10.1039/C3DT51681D C₃₁H₆₀GeN₂O₅Si₂ (669.63 g·mol⁻¹): theoretical, C 55.6%, H 9.0%, N 4.2%; found C 55.5%, H 8.9%, N 4.1%.

{LO³}GeCl. A solution of {LO³}K (0.50 g, 1.05 mmol) in THF (20 mL) was added dropwise to a solution of GeCl₂ dioxane (0.25 g, 1.06 mmol) in THF (30 mL). The reaction mixture was stirred overnight at room temperature. After removal of the volatiles at low pressure, the crude product was extracted with Et₂O (3×7 mL) and dried *in vacuo* to give the title compound (0.41 g, 72%) as a colourless solid. Single crystals of {LO³} GeCl were grown from a concentrated toluene solution at room temperature and their structure was solved. ¹H NMR (benzene-*d*₆, 298 K, 500.13 MHz,): δ = 7.58 (d, ⁴*J*_{HH} = 2.5 Hz, 1H, aromatic-*H*), 6.78 (d, ⁴*J*_{HH} = 2.5 Hz, 1H, aromatic-*H*), 4.30–2.39 (m, 24H, all NC*H*₂ and OC*H*₂), 1.70 (s, 9H, C(C*H*₃)₃), 1.37 (s, 9H, C(C*H*₃)₃) ppm; ¹³C {¹H} NMR (benzene-*d*₆, 298 K, 125.76 MHz): δ = 155.02, 140.73, 139.42, 125.42, 124.85 and 120.75 (all aromatic-*C*), 71.43, 71.25, 70.44, 70.31, 66.42, 65.60 and 57.11 (all NCH₂ and OCH₂), 54.89 (ArC*H*₂N), 53.03 and 51.32 (NCH₂CH₂O), 35.42 and 34.37 (both *C*(CH₃)₃), 32.00 and 30.46 (both C(*C*H₃)₃) ppm. Elemental analysis for C₂₅H₄₂ClGeNO₅ (544.70 g·mol⁻¹): theoretical, C 55.1%, H 7.8%, N 2.6%; found C 54.9%, H 7.6%, N 2.5%.

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 $\{LO^4\}Sn(N(SiMe_3)_2)$ (8). A solution of $\{LO^4\}H$ (0.20 g, 0.50 mmol) in diethyl ether (20 mL) was added at -80 °C over a period of 30 min to a solution of $Sn(N(SiMe_3)_2)_2$ (0.22 g, 0.51 mmol) in diethyl ether (20 mL). The colour of the solution rapidly changed from deep orange to yellow. The resulting mixture was warmed to room temperature and the volatiles were removed under vacuum. The resulting powder was washed with cold pentane (2 mL) at -20 °C and dried *in vacuo* to give 8 as a white powder (0.19 g, 57%). Single-crystals of 8 suitable

for X-ray diffraction were obtained by recrystallisation from a cold mixture of pentane and were obtained by recrystallisation from a cold mixture of pentane and were obtained by recrystallisation from a cold mixture of pentane and were obtained by recrystallisation from a cold mixture of pentane and were obtained by recrystallisation from a cold mixture of pentane and were obtained by recrystallisation from a cold mixture of pentane and were obtained by recrystallisation from a cold mixture of pentane and were obtained by recrystallisation from a cold mixture of pentane and were obtained by recrystallisation from a cold mixture of pentane and were obtained by recrystallisation from a cold mixture of pentane and were obtained by recrystallisation from a cold mixture of pentane and were obtained by recrystallisation from a cold mixture of pentane and were obtained by recrystallisation from a cold mixture of pentane and were obtained by recrystallisation from a cold mixture of pentane and were obtained by recrystallisation from a cold mixture of pentane and were obtained by recrystallisation from a cold mixture of pentane and were obtained by recrystallisation from a cold mixture of pentane and were obtained by recrystallisation from a cold mixture of pentane and were obtained by recrystallisation from a cold mixture of pentane analysis for C20: $\delta = 7.55$ (d, $^4J_{HH} = 2.5$ Hz, 1H, aromatic-H), 6.91 (d, $^4J_{HH} = 2.5$ Hz, 1H, aromatic-H), and $P_1 = 2.5$ Hz, 1H, aromatic-H, and $P_2 = 2.5$ Hz, 1H, aromatic-H, $P_1 = 2.5$ Hz, 1H, aromatic-H, $P_2 = 2.5$ Hz, $P_1 = 2.5$ Hz, $P_2 = 2.56$ (by $P_1 = 2.56$ (by $P_2 = 2.56$ (by $P_2 = 2.56$ (by $P_1 = 2.56$ (b), $P_2 = 2.56$ (b), P_2

{**LO**³}**SnCl.** A solution of {LO³}K (0.48 g, 1.00 mmol) in THF (20 mL) was added dropwise to a solution of SnCl₂ (0.19 g, 1.01 mmol)in THF (30 mL). The reaction mixture was stirred overnight at room temperature. After removal of the volatiles at low pressure, the crude product was extracted with Et₂O (3×7 mL) and dried *in vacuo* to give the title compound (0.32 g, 54%) as a colourless solid. ¹H NMR (benzene-*d*₆, 298 K, 400.13 MHz,): δ = 7.64 (d, ⁴*J*_{HH} = 2.4 Hz, 1H, aromatic-*H*), 6.80 (d, ⁴*J*_{HH} = 2.4 Hz, 1H, aromatic-*H*), 3.83(m, 2H, ArC*H*₂N), 3.61–3.56 (m, 2H, NC*H*₂CH₂), 3.30–3.23 (m, 6H, OC*H*₂), 3.11–3.07 (m, 8H, OC*H*₂), 2.97–2.95 (m, 2H, OC*H*₂), 2.33–2.30 (m, 2H, NC*H*₂CH₂), 1.78 (s, 9H, C(C*H*₃)₃), 1.43 ppm (s, 9H, C(C*H*₃)₃); ¹³C{¹H} NMR (benzene-*d*₆, 298 K, 100.62 MHz): δ = 160.00, 139.30, 138.39, 126.63, 125.12 and 122.20 (all aromatic-*C*), 70.91, 70.51 and 67.13 (all OCH₂), 61.00 (NCH₂CH₂), 54.11 (ArC*H*₂N), 36.01 and 34.72 (both *C*(CH₃)₃), 32.68 and 30.95 (both C(*C*H₃)₃) ppm; ¹¹⁹Sn{¹H} NMR (toluene-*d*₈, 149.20 MHz, 25 °C): δ –385.0 ppm. Elemental Transactions Accepted Manuscript

analysis for $C_{25}H_{42}CINO_5Sn (590.77 \text{ g} \cdot \text{mol}^{-1})$: theoretical, C 50.8%, H 7.2%, N 2.4%. For the online Doi: 10.1039/C3DT51681D C 50.9%, H 7.2%, N 2.4%.

{LO¹}Pb(N(SiMe₃)₂) (9). Following a protocol similar to that described for **1**, the reaction of {LO¹}H (0.42 g, 1.20 mmol) and Pb(N(SiMe₃)₂)₂ (0.64 g, 1.22mmol) afforded **9** as a white powder (0.72 g, 84%). Single-crystals of **9** suitable for X-ray diffraction were obtained by recrystallisation from a cold mixture of pentane and diethyl ether. ¹H NMR (toluene-*d*₈, 500.13 MHz, 25 °C): δ = 7.62 (d, 1H, ⁴*J*_{HH} = 2.5 Hz, aromatic-*H*), 6.93 (d, 1H, ⁴*J*_{HH} = 2.5 Hz, aromatic-*H*), 3.93–3.89 (br m, 4H, ArC*H*₂N and NC*H*₂CH₂), 3.41–2.99 (dt, 4H, ³*J*_{HH} = 10.5 Hz, NCH₂C*H*₂O), 2.91 (br, 2H, NC*H*₂CH₂), 2.85 (s, 6H, OC*H*₃), 1.68 (s, 9H, C(C*H*₃)₃), 1.39 (s, 9H, C(C*H*₃)₃), 0.43 (s, 18H, N(Si(C*H*₃)₃)₂) ppm. ¹³C {¹H} NMR (toluene-*d*₈, 125.76 MHz, 25 °C): δ = 161.00, 140.90, 137.80, 126.97,124.73 and 124.68 (all aromatic-*C*), 68.30 (OCH₂), 58.48(OCH₃), 57.74(ArCH₂N), 51.78(NCH₂CH₂), 35.58 (*C*(CH₃)₃), 34.34 (*C*(C(H₃)₃), 32.51 (C(CH₃)₃), 30.98 (C(CH₃)₃), 7.19 (N(Si(CH₃)₃)₂) ppm. ²⁹Si {¹H} NMR (toluene-*d*₈, 83.71 MHz, 25 °C): δ = -3.35 ppm. ²⁰⁷Pb {¹H} NMR (toluene-*d*₈, 83.71 MHz, 25 °C): δ _{Pb} = +2007 ppm. Elemental analysis for C₂₇H₅₄N₂O₃PbSi₂ (718.10 g·mol⁻¹): theoretical, C 45.2%, H 7.6%, N 3.9%; found C 44.9%, H 7.4%, N 3.7%.

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{ LO^{2} }Pb(N(SiMe₃)₂) (10). Following a protocol similar to that described for 1, the reaction of { LO^{2} }H (0.35 g, 1.20 mmol) and Pb(N(SiMe₃)₂)₂ (0.64 g, 1.22mmol) afforded 10 as a colourless powder (0.65 g, 81%). Single-crystals suitable of 10 for X-ray diffraction were obtained by recrystallisation from a cold mixture of pentane and toluene.¹H NMR (toluene-*d*₈, 400.13 MHz, 25 °C): δ = 7.61 (d, 1H, ⁴*J*_{HH} = 2.5 Hz, aromatic-*H*), 6.86 (d, 1H, ⁴*J*_{HH} = 2.5 Hz, aromatic-*H*), 4.15 (br, 1H, ArC*H*₂N), 3.22–3.10 (br m, 2H, NC*H*₂CH₃), 2.79 (br, 1H, ArC*H*₂N), 2.44–2.33 (br m, 2H, NC*H*₂CH₃), 1.67 (s, 9H, C(C*H*₃)₃), 1.40 (s, 9H, C(C*H*₃)₃),

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0.74 and 0.57 (br m, 6H, both NCH₂CH₃), 0.39 ppm (s, 18H, N(Si(CH₃)₃)₂). ¹³C {¹H}_{DOI}, NMER Article Online (toluene-*d*₈, 100.62 MHz, 25 °C): δ =160.68, 140.97, 138.48, 126.84, 124.93 and 124.79 (all aromatic-*C*), 56.28 (ArCH₂N), 46.27 and 43.68 (both NCH₂CH₃), 35.56 and 34.38 (both C(CH₃)₃), 32.47 and 30.88 (both C(CH₃)₃), 10.19 and 7.48 (both NCH₂CH₃), 7.01ppm (N(Si(CH₃)₃)₂). ²⁹Si {¹H} NMR (toluene-*d*₈, 79.49 MHz, 25 °C): δ = -2.35 ppm. ²⁰⁷Pb {¹H} NMR (toluene-*d*₈, 83.71 MHz, 25 °C): δ = 2109 ppm. Elemental analysis for C₂₅H₅₀N₂OPbSi₂ (658.05 g.mol⁻¹): theoretical, C 45.6%, H 7.7%, N 4.3%; found C 45.4%, H 7.8%, N 4.2%.

 $\{LO^3\}Pb(N(SiMe_3)_2)$ (11). Following a protocol similar to that described for 1, the reaction of $\{LO^3\}H$ (0.42 g, 0.96 mmol) and Pb(N(SiMe_3)_2)_2 (0.52 g, 0.96 mmol) afforded after extended work-up a mixture of **11** (90%) and $\{LO^3\}_2Pb$ (10%) which could not be purified. X-ray quality crystals of 11 were obtained by recrystallisation from pentane at room temperature. Spectroscopic data for **11** (see below for analytically pure $\{LO^3\}_2Pb$): ¹H NMR (benzene- d_6 , 400.13 MHz, 25 °C): $\delta = 7.71$ (d, ${}^4J_{\text{HH}} = 2.8$ Hz, 1H, aromatic-H), 6.98 (d, ${}^4J_{\text{HH}} =$ 2.8 Hz, 1H, aromatic-H), 3.87 (br, 2H, ArCH₂N and OCH₂), 3.80-3.74 (m, 2H, OCH₂), 3.41-3.38 (m, 2H, OCH₂ and ArCH₂N), 3.24–3.18 (m, 12H, OCH₂ and NCH₂CH₂), 3.03 (br, 4H, OCH₂), 1.77 (s, 9H, C(CH₃)₃), 1.44 (s, 9H, C(CH₃)₃), 0.52 (s, 18H, N(Si(CH₃)₃)₂)₂ ppm. ¹³C{¹H} NMR (benzene- d_6 , 100.61 MHz, 25 °C): $\delta = 161.43$, 141.13, 138.25, 127.22, 125.45 and 124.78 (all aromatic-C), 71.35, 70.83, 70.58 and 67.36 (OCH₂), 58.87 (ArCH₂N), 53.51(NCH₂CH₂), 35.90 and 34.60 (both C(CH₃)₃), 32.81 and 31.42 (both C(CH₃)₃), 7.32 $(N(Si(CH_3)_3)_2) \text{ ppm.}^{29}Si\{^{1}H\} \text{ NMR (benzene-}d_6, 79.49 \text{ MHz, } 25 \text{ °C}): \delta = -3.29 \text{ ppm.}$ 207 Pb{ 1 H}NMR (benzene-*d*₆, 83.71 MHz, Pb(N(SiMe₃)₂)₂, 25 °C): $\delta = +2027$ ppm. Elemental analysis for $C_{31}H_{60}N_2O_5PbSi_2$ (804.19 g·mol⁻¹) could not be obtained owing to contamination with $\{LO^3\}_2Pb$.

[LO³]₂Pb. A solution of {LO³}H (0.53 g, 1.21 mmol) in Et₂O (15 mL) was added, therefore online solution of Pb(N(SiMe₃)₂)₂ (0.32 g, 0.60 mmol) in Et₂O (15 mL). In seconds a white precipitate was formed. The reaction mixture was stirred overnight. The precipitate was isolated by filtration, washed with Et₂O (3 × 5 mL) and dried under reduced pressure to give {LO³}₂Pb (0.39 g, 60%) as a colourless solid. Single-crystals of {LO³}₂Pb·C₆H₆ were grown from benzene and their structure was determined. ¹H NMR (benzene-*d*₆, 500.25 MHz, 25 °C): $\delta = 7.80$ (d, ⁴*J*_{HH} = 3.0 Hz, 1H, aromatic-*H*), 7.40 (d, ⁴*J*_{HH} = 3.0 Hz, 1H, aromatic-*H*), 5.45 (br, 1H, ArCH₂N), 3.54–2.93 (m br, 21H, ArCH₂N, OCH₂ and NCH₂CH₂), 1.85 (s, 9H, C(CH₃)₃), 1.52 (s, 9H, C(CH₃)₃) ppm. ¹³C{¹H} NMR (benzene-*d*₆, 125.76 MHz, 25 °C): $\delta = 164.15$, 138.45, 135.16, 128.79, 128.16 and 124.40 (all aromatic-*C*), 70.72, 70.55 (br), 69.98 (br), 68.79 (all NCH₂CH₂ and OCH₂), 61.13 (ArCH₂N), 36.06 and 34.57 (both *C*(CH₃)₃), 32.93 (C(CH₃)₃) and 30.94 (both C(CH₃)₃) ppm. ²⁰⁷Pb NMR (benzene-*d*₆, 83.71 MHz, 60 °C): $\delta = -367$ ppm. Elemental analysis for C₅₀H₈₄N₂O₁₀Pb (1080.41 g·mol⁻¹): theoretical, C 55.6%, H 7.8%, N 2.6%.

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[LO³]H·LiOTf. In a Schlenk vessel, a mixture of LiOTf (0.25 g, 1.60 mmol) and {LO³}H (0.72 g, 1.65 mmol) was suspended in diethyl ether (20 mL). Upon stirring at room temperature, all LiOTf dissolved to give a clean, colourless solution. The volatiles were then removed under vacuum to quantitatively give analytically pure **{LO³}H·LiOTf** (0.97 g, 100%) as a colourless powder. Crystals suitable for X-ray diffraction studies of the title compound were rapidly obtained upon layering a hot solution in diethyl ether with pentane and gentle cooling to room temperature. ¹H NMR (benzene-*d*₆, 400.13 MHz, 25 °C): δ = 10.01 (s, 1H, aromatic-OH), 7.47 (d, ⁴*J*_{HH} = 4.0 Hz, 1H, aromatic-*H*), 6.89 (d, ⁴*J*_{HH} = 4.0 Hz, 1H, aromatic-*H*), 3.40–3.15 (m, 18H, ArC*H*₂N, OC*H*₂ and NC*H*₂CH₂), 2.37 (br s, 4H, OC*H*₂), 1.57 (s, 9H, C(C*H*₃)₃), 1.37 (s, 9H, C(C*H*₃)₃) ppm. ¹³C {¹H} NMR (benzene-*d*₆, 100.62

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MHz, 25 °C): $\delta = 154.37$ (*i*-*C*), 141.09 (*p*-*C*), 135.72 (*o*-*C*), 124.20 (*o*-*C*), 123.15 (*m*-*C*), View Article Online Dol: 10.1039/C3DT51681D 122.26 (*m*-*C*), 121.3 (q, CF₃, ¹*J*_{CF} = 319 Hz), 68.93, 68.10, 67.65, and 66.89 (all OCH₂), 58.01 (ArCH₂N), 50.90 (NCH₂CH₂), 35.20 and 34.38 (both *C*(CH₃)₃), 31.99 and 29.99 (both C(CH₃)₃). ⁷Li NMR (155.51 MHz, 25 °C): in benzene- d_{6} , $\delta = -0.96$ ppm; in dichloromethane- d_{2} , -0.84 ppm. ¹⁹F NMR (benzene- d_{6} , 376.45 MHz, 25 °C): $\delta = -77.98$ (s, 3F) ppm. Elemental analysis for C₂₆H₄₃F₃LiNO₈S (593.62 g·mol⁻¹): theoretical, C 52.6%, H 7.3%, N 2.4%; found C 52.7%, H 7.2%, N 2.4%.

{LO³}Ge(N(SiMe₃)₂)·LiOTf (3·LiOTf). CF₃SO₃Li (47 mg, 0.29 mmol) was added to a solution of {LO³}Ge(N(SiMe₃)₂) (0.20 g, 0.3 mmol) in Et₂O (15 mL). After stirring the reaction mixture for 30 min, the volatiles were removed *in vacuo* to afford **3·LiOTf** (220 mg, 89%) as a white powder. The compound still contained *ca*. 8% of $\{LO^3\}H\cdot LiOTf$ and the mixture could not be further separated. A small crop of X-ray quality crystals of 3. LiOTf was grown by recrystallisation from a concentrated diethyl ether solution at room temperature. ¹H NMR (benzene- d_6 , 400.13 MHz, 25 °C): δ = 7.61 (d, ${}^4J_{HH}$ = 1.8 Hz, 1H, aromatic-H), 7.18 (d, ${}^{4}J_{\text{HH}} = 1.8 \text{ Hz}, 1\text{H}, \text{ aromatic-}H), 3.86-3.09 (br m, 22\text{H}, ArCH_2N, NCH_2CH_2 \text{ and OCH}_2),$ 1.65(s, 9H, C(CH₃)₃), 1.39 (s, 9H, C(CH₃)₃), 0.43 (br s , 18H, N(Si(CH₃)₃)₂). ¹³C{¹H} NMR (benzene- $d_6/1, 2-C_6H_4F_2 = 5:2, 100.62 \text{ MHz}, 25 \text{ °C}$): $\delta = 156.84, 142.48, 141.62, 128.79, \delta = 126.84, 142.48,$ 127.45 and 125.92 (all aromatic-C), 121.00 (q, CF_3 , ${}^1J_{CF} = 320$ Hz), 70.26–70.01, 68.14– 67.96 and 67.49-67.37 (all NCH₂CH₂, OCH₂), 56.82 (ArCH₂N), 35.64 and 34.92 (both $C(CH_3)_3$, 32.32 and 31.19 (both $C(CH_3)_3$), 7.34 and 6.03 (br, both $N(Si(CH_3)_3)_2$) ppm. ²⁹Si{¹H} NMR (toluene- d_8 , 79.49 MHz, 40 °C): $\delta = +0.70$ ppm. ⁷Li NMR (benzene- d_6 , 155.51 MHz, 25 °C): $\delta = -0.74$ ppm. ¹⁹F NMR (benzene-*d*₆, 376.45 MHz, 25 °C): $\delta = -77.92$ (s, 3F) ppm. Elemental analysis for $C_{32}H_{60}F_{3}GeLiN_{2}O_{8}SSi_{2}$ (825.64 g·mol⁻¹) could not be obtained owing to contamination with $\{LO^3\}H\cdot LiOTf$.

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{LO³}Sn(N(SiMe₃)₂)-LiOTf (7·LiOTf). CF₃SO₃Li (47 mg, 0.29 mmol) was added in portions with a bent finger to a solution of {LO³}Sn(N(SiMe₃)₂) (0.21g, 0.3 mmol) in Et₂O (20 mL). After stirring the reaction mixture for 30 min, the volatiles were removed at low pressure to afford **7·LiOTf** (200 mg, 78%) as a white powder. Single-crystals of **7·LiOTf** were obtained by recrystallisation from a mixture of THF and toluene at room temperature. ¹H NMR (CD₂Cl₂, 500.13 MHz, 25 °C): *δ* = 7.34 (d, ⁴*J*_{HH} = 2.5 Hz, 1H), 6.95 (d, ⁴*J*_{HH} = 2.5 Hz, 1H), 4.34–3.14 (br m, 24H, ArC*H*₂N, OC*H*₂ and NC*H*₂CH₂), 1.43 (s, 9H, C(C*H*₃)₃), 1.29 (s, 9H, C(C*H*₃)₃), 0.27 (s, 18H, N(Si(C*H*₃)₃)₂) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 125.76 MHz, 25 °C): *δ* = 158.44, 140.51, 129.39, 127.40, 125.25 and 124.15 (all aromatic-C), 120.79 (q, CF₃, ¹*J*_{CF} = 319 Hz), 70.21 and 67.94 (br, OCH₂ and NCH₂CH₂), 56.62 (ArCH₂N), 35.08 and 34.39 (both *C*(CH₃)₃), 31.80 and 30.30 (both C(CH₃)₃), 6.44 (N(Si(CH₃)₃)₂) ppm. ¹¹⁹Sn{¹H} NMR (CD₂Cl₂, 149.20 MHz, 25 °C): *δ* = −45.8 ppm; ⁷Li{¹H} NMR (CD₂Cl₂, 155.51 MHz, 25 °C): *δ* = −0.56 ppm. ¹⁹F NMR (376.45 MHz, C₆D₆, 25 °C) *δ* = −78.78 (s, 3F) ppm. ²⁹Si{¹H} NMR (CD₂Cl₂, 79.49 MHz, 25 °C): *δ* = −0.31 ppm. Elemental analysis for C₃₂H₆₀F₃LiN₂O₈SSi₂Sn (871.71 g·moΓ⁻¹): theoretical, C 44.1%, H 6.9%, N 3.2%; found C 44.0%, H 6.9%, N 3.3%.

Typical polymerisation procedure. In the glove-box, the metal initiator was placed in a Schlenk flask together with the monomer and magnetic stirring bar. The Schlenk flask was sealed and removed from the glove box. All subsequent operations were carried out on a vacuum manifold using Schlenk techniques. The required amount of dry, degassed solvent was added with a syringe to the catalyst and the monomer, followed when required by addition of the chain-transfer agent (*i*PrOH). Depending on the need, the resulting mixture was immerged in an oil bath pre-set at the desired temperature or in an iced-water bath, and the polymerisation time was measured from this point. The reaction was terminated by

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addition of acidified MeOH (HCl, 1 wt-%) and the polymer was precipitated in methano View Article Online bol: 10.1039/C3DT51681D washed thoroughly. The polymer was then dried to constant weight in a vacuum oven at 55 °C under dynamic vacuum ($<5 \cdot 10^{-2}$ mbar).

X-ray diffraction crystallography. Crystals of 1–3, 8–11, {LO³}GeCl, {LO³}SnCl, ${LO^{3}}_{2}Pb \cdot C_{6}H_{6}$, ${LO^{3}}H \cdot LiOTf$, **3·LiOTf** and **7·LiOTf** suitable for X-ray diffraction analysis were obtained by recrystallization of the purified products. Diffraction data were collected at 150 K using a Bruker APEX CCD diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). A combination of ω and Φ scans was carried out to obtain at least a unique data set. The crystal structures were solved by direct methods, remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares refinement based on F2 (programs SIR97 and SHELXL-97).⁴⁶ Many hydrogen atoms could be found from the Fourier difference analysis. Carbon- and oxygen-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. The hydrogen atom contributions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities were of no chemical significance. Relevant collection and refinement data are summarised in Tables 5-8. Crystal data and details of data collection and structure refinement for all complexes (CCDC 942087-942099) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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Electronic supplementary information (ESI) available: VT NMR data and details of line-

shape analysis for **2**, **10** and $\{LO^2\}$ SnCl; X-ray structure of $\{LO^3\}_2$ Pb·C₆H₆.

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Table 5. Summary of crystallographic data for 1-3

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	${LO^1}Ge(N(SiMe_3)_2)$	{LO ² }Ge(N(SiMe ₃) ₂)	{LO ³ }Ge(N(SiMe ₃) ₂)
	1	2	3
Formula	$C_{27}H_{54}GeN_2O_3Si_2$	C25H50GeN2OSi2	$C_{31}H_{60}GeN_2O_5Si_2$
CCDC	942087	942089	942093
Mol. wt.	583.49	523.44	669.63
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P 2 ₁ /n	P-1	$P 2_1/n$
a(Å)	13.4042(4)	10.4714(6)	13.0369(18)
$b(\text{\AA})$	17.7120(4)	12.3029(8)	15.596(2)
$c(\text{\AA})$	13.8889(4)	12.3573(6)	18.084(3)
<i>α</i> (°)	90	81.087(3)	90
β(°)	99.1210(10)	75.381(2)	98.921(6)
γ(°)	90	86.021(3)	90
V(Å ³)	3255.74(15)	1521.07(15)	3632.4(9)
Ζ	4	2	4
Density (g/cm ³)	1.19	1.143	1.224
Abs. coeff., (mm ⁻¹)	1.042	1.103	0.947
<i>F</i> (000)	1256	564	1440
Crystal size, mm	0.6×0.3×0.25	0.32×0.23×0.15	0.17×0.12×0.07
θ range, deg	3.02 to 27.48	2.95 to 27.49	3.05 to 27.48
	-17 < h < 17	-13 < h < 13	$-16 \le h \le 14$
Limiting indices	-2 < k < 22	-15 < k < 15	-17 < k < 20
	-14 < l < 18	-16 < 1 < 16	-22 < 1 < 23
<i>R</i> (int)	0.0388	0.0465	0.0355
Reflections collected	19774	25015	29717
Reflec. Unique $[I > 2\sigma(I)]$	5797	5730	8212
Completeness to θ	0.995	0.993	0.987
Data/restraints/param.	7420 / 0 / 330	6928 / 0 / 294	8212 / 0 / 382
Goodness-of-fit	1.051	1.064	1.021
$R_1[I \ge 2\sigma(I)]$ (all data)	0.0512 (0.123)	0.0352 (0.0777)	0.0287 (0.0388)
w R_2 [$I > 2\sigma(I)$] (all data)	0.0697 (0.1325)	0.0465 (0.0818)	0.0675 (0.0719)
Largest diff. e·A ⁻³	1.723 and -0.777	0.431 and –0.271 3	0.371 and -0.212

Table 6.	Summary	of crystallog	raphic data	1 for 9–11	and {	$\{LO^3\}_2Pb.C$	6H ₆ .
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	$\{LO^3\}_2Pb.C_6H_6$	$\{LO^1\}Pb(N(SiMe_3)_2)$	${LO2}Pb(N(SiMe_3)_2)$	${LO^3}Pb(N(SiMe_3)_2)$
		9	10	11
Formula	$C_{56}H_{90}N_2O_{10}Pb$	$C_{27}H_{54}N_2O_3PbSi_2$	$C_{25}H_{50}N_2O_1PbSi_2$	$C_{31}H_{60}N_2O_5PbSi_2$
CCDC	942091	942088	942090	942096
Mol. wt.	1158.49	718.09	658.04	804.19
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	P 2 ₁ /n	P-1	P-1	P-1
a(Å)	14.0101(4)	10.5521(10)	10.5366(4)	12.1963(3)
$b(\text{\AA})$	27.8363(7)	13.7269(13)	11.8539(4)	12.2480(4)
$c(\text{\AA})$	14.9256(4)	15.0466(12)	12.2084(4)	14.3540(3)
α(°)	90	64.082(3)	87.436(2)	66.5600(10)
$\beta(^{\circ})$	101.4870(10)	69.863(3)	81.9730(10)	68.9620(10)
γ(°)	90	81.892(3)	87.2970(10)	75.4680(10)
$V(Å^3)$	5704.2(3)	1840.3(3)	1507.08(9)	1821.43(8)
Ζ	4	2	2	2
Density (g/cm ³)	1.349	1.296	1.45	1.466
Abs. coeff., (mm ⁻¹)	3.013	4.673	5.694	4.734
<i>F</i> (000)	2408	728	664	820
Crystal size, mm	0.35×0.1×0.09	0.1×0.1×0.1	0.26×0.21×0.12	0.54×0.23×0.19
θ range, deg	2.93 to 27.44	2.93 to 27.49	3.04 to 27.48	2.96 to 27.48
	-16 < h < 18	-13 < h < 13	-13 < h < 13	-15 < h < 15
Limiting indices	-33 < k < 36	-17 < k < 17	-13 < k < 15	-15 < k < 15
	-19 < l < 19	-19 < 1 < 19	-15 < 1 < 15	-17 < l < 18
<i>R</i> (int)	0.0354	0.052	0.0367	0.0413
Reflections collected	48821	17711	15900	20820
Reflec. Unique $[I > 2\sigma(I)]$	12869	6343	5938	8228
Completeness to θ	0.988	0.973	0.985	0.985
Data/restraints/param.	12869 / 0 / 634	8232 / 0 / 330	6818 / 0 / 294	8228 / 0 / 382
Goodness-of-fit	1.012	0.998	1.009	1.012
$R_1[I \ge 2\sigma(I)]$ (all data)	0.029 (0.046)	0.0499 (0.1108)	0.0306 (0.0547)	0.0269 (0.0321)
w $R_2 [I > 2\sigma(I)]$ (all data)	0.0572 (0.0617)	0.0693 (0.1172)	0.0391 (0.0569)	0.0558 (0.0574)
Largest diff. e · A ⁻³	0.918 and -0.81	2.093 and -2.096	0.9 and -0.9	0.6 and -1.159

{LO³}SnCl

Formula	$C_{29}H_{56}N_2O_4Si_2Sn$	$C_{25}H_{42}ClNO_5Sn$	C25H42ClGeNO5
CCDC	942099	942097	942092
Mol. wt.	671.63	590.74	544.64
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P –1	P ₂ /n	P 2 ₁ /n
a(Å)	10.7245(3)	14.4474(6)	14.4685(7)
$b(\text{\AA})$	13.2277(4)	10.9372(5)	10.9550(5)
$c(\text{\AA})$	13.3588(4)	18.6881(7)	18.4462(10)
$\alpha(^{\circ})$	70.5920(10)	90	90
$\beta(^{\circ})$	85.7950(10)	111.8890(10)	112.213(2)
γ(°)	77.0520(10)	90	90
$V(Å^3)$	1741.95(9)	2740.1(2)	2706.8(2)
Ζ	2	4	4
Density (g/cm ³)	1.28	1.432	1.336
Abs. coeff., (mm ⁻¹)	0.834	1.063	1.264
<i>F</i> (000)	708	1224	1152
Crystal size, mm	0.38×0.34×0.14	0.56×0.18×0.08	0.6×0.12×0.04
θ range, deg	2.97 to 27.46	2.91 to 27.48	2.93 to 27.48
	-12 < h < 13	-18 < h < 18	$-18 \le h \le 17$
Limiting indices	-17 < k < 17	$-12 \le k \le 14$	$-12 \le k \le 14$
	-17 < 1 < 17	-17 < 1 < 24	-23<1<23
<i>R</i> (int)	0.0243	0.0435	0.0538
Reflections collected	21981	22244	23337
Reflec. Unique $[I > 2\sigma(I)]$	7123	5399	4638
Completeness to θ	0.98	0.996	0.999
Data/restraints/param.	7802 / 0 / 355	6259 / 0 / 304	6197 / 0 / 308
Goodness-of-fit	1.026	1.024	1.081
$R_1[I > 2\sigma(I)]$ (all data)	0.0219 (0.05)	0.0307 (0.0707)	0.0412 (0.1005)
w $R_2[I > 2\sigma(I)]$ (all data)	0.0258 (0.0516)	0.0384 (0.0748)	0.065 (0.1164)
Largest diff. e·A ⁻³	0.338 and -0.272	1.418 and -0.574	1.087 and -0.862

Table 7. Summary of crystallographic data for **8**, $\{LO^3\}$ GeCl and $\{LO^3\}$ SnCl.

 $\{LO^4\}Sn(N(SiMe_3)_2$

8

{LO3}GeCl

	{LO ³ }H.LiOTf	{LO ³ }Ge(N(SiMe ₃) ₂)·CF ₃ SO ₃ Li	{LO ³ }Sn(N(SiMe ₃) ₂)·CF ₃ SO ₃ Li
		3·LiOTf	7·LiOTf
Formula	C ₂₆ H ₄₃ F ₃ LiNO ₈ S	$C_{32}H_{60}F_3GeLiN_2O_8SSi_2$	$C_{32}H_{60}F_3LiN_2O_8SSi_2Sn$
CCDC	942095	942094	942098
Mol. wt.	593.61	825.59	871.69
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P 2_1/n$	P-1	P-1
a(Å)	9.4732(13)	9.1913(2)	8.8219(2)
b(Å)	27.781(4)	11.3799(2)	11.8940(2)
c(Å)	12.5458(14)	21.3025(4)	21.6592(3)
α(°)	90	97.0250(10)	74.5550(10)
β(°)	109.382(6)	100.1770(10)	78.5080(10)
γ(°)	90	98.1600(10)	80.5870(10)
V(Å ³)	3114.6(7)	2145.92(7)	2131.92(7)
Ζ	4	2	2
Density (g/cm ³)	1.266	1.278	1.358
Abs. coeff., (mm ⁻¹)	0.166	0.875	0.762
<i>F</i> (000)	1264	872	908
Crystal size, mm	0.58×0.46×0.21	0.18×0.12×0.07	0.35×0.18×0.12
θ range, deg	1.47 to 27.46	2.91 to 27.46	2.92 to 27.48
	-12 < h < 11	-11 < h < 11	-11 < h < 11
Limiting indices	0 < k < 36	-14 < k < 14	-15 < k < 15
<i>R</i> (int)	0 < l < 16 0.0000	-27 < 1 < 27 0.0334	-24 < 1 < 28 0.0329
Reflections collected	7023	34506	22861
Reflec. Unique $[I > 2\sigma(I)]$	7023	9720	8442
Completeness to θ	0.980	0.991	0.988
Data/restraints/param.	7023 / 0 / 382	9720 / 0 / 463	9691 / 0 / 463
Goodness-of-fit	1.078	1.032	1.023
$R_1[I > 2\sigma(I)]$ (all data)	0.0590 (0.0847)	0.0332 (0.0448)	0.0324 (0.0706)
w $R_2[I > 2\sigma(I)]$ (all data)	0.1599 (0.1817)	0.0763 (0.0813)	0.0397 (0.0742)
Largest diff. e·A ⁻³	0.391 and -0.488	0.491 and -0.341	0.439 and -0.355

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Stable Divalent Germanium, Tin and Lead Amino(ether)-phenolate Monomeric Complexes: Structural Features, Inclusion Heterobimetallic Complexes, and ROP Catalysis

Lingfang Wang, Sorin-Claudiu Roşca, Valentin Poirier, Sourisak Sinbandhit, Vincent Dorcet, Thierry Roisnel, Jean-François Carpentier and Yann Sarazin*

Stable, monomeric germylenes, stannylenes and plumbylenes bearing amino(ether)-phenolate ligands, including some heterobimetallic alkali complexes, catalyse the controlled ring-opening polymerisation of lactide.